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MM&T PROGRAM TO ESTABLISH PRODUCTION
TECHNIQUES FOR THE AUTOMATIC DETECTION
AND QUALIFICATION OF TRACE ELEMENTS PRESENT
IN THE PRODUCTION OF MICROWAVE
SEMICONDUCTORS

SECOND QUARTERLY REPORT
23 November 1977 to 28 February 1978

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Production Division, Procurement and Production Directorate
USAECOM, Fort Monmouth, New Jersey 07703

Contract DAAB07-77-C-0561

Harris Corporation, PRD Electronics Division
6801 Jericho Turnpike, Syosset, New York 11791

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MM&T PROGRAM TO ESTABLISH PRODUCTION
TECHNIQUES FOR THE AUTOMATIC DETECTION
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SEMICONDUCTORS.

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SECOND QUARTERLY REPORT. no. 29

23 November 1977 to 28 February 1978

Object of Study

Establish production technique for the automatic detection and concentration quantification of the trace elements (impurities) in the organic and inorganic compounds and solutions that are used in the fabrication of microwave semiconductors and the determination of acceptable impurity levels.

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Contract No.: DAAB07-77-C-0561

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Report Prepared by: Roy W. Spacie

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19. ABSTRACT (Continue on reverse side if necessary and identify by block number) A project was undertaken to improve the yield in the manufacture of microwave semiconductor diodes by establishing the correlation of product yields to the incidence of contaminants in the reagents and solvents used in the manufacturing process and using these data to model the process for optimization of the yield.		

ABSTRACT

This is the second quarterly progress report of a US Army sponsored study which had as its objective the improvement of product yields in the manufacture of microwave semiconductor devices by establishing the correlation between the electrical performance of such devices and the levels of trace element contamination in the materials used in the manufacturing process. The quarter primarily was devoted to the acquisition, assembly and calibration of the analytic tools to be used and the training of operating personnel and the development of computer programs for the statistical analysis of the test data.

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GLOSSARY

Aliquot:	contained an exact number of times in another, fractional.
Analysis of Covariance:	a statistical technique that combines the features of variance and regression.
Analytic Model:	a set of equations and/or logic statements, generally implemented on a computer, which quantitatively represents the interrelationships that characterize a given system.
Angstrom:	A unit of length (wavelength) equal to one ten-billionth of a meter, i.e., 10^{-10} m.
Boule:	a pear-shaped mass formed synthetically in a special furnace with the atomic structure of a single crystal.
Clustering:	statistical procedures which classify data into recognizable sub-groups according to a defined criterion function.
Factor Analysis:	a statistical procedure to find a lower-dimensional representation that accounts for the correlation among variables.
Epitaxial:	having orientation controlled by the crystalline substrate - used of crystals and of the relationship between them and their substrate.
Ionize:	to cause a change in the number of electrons in the outer orbits of an atom such that it exhibits a net electrical charge.
Matrix:	that within which something else originates or develops, e.g., a format for developing computer instructions.
Mesa:	(~ transistor) structured as a mesa - an isolated hill having steeply sloping sides and a level top.
Nanogram:	one billionth of a gram. (Also used are femtogram [one quadrillionth], picogram [one trillionth] and microgram [one millionth].)

GLOSSARY (Contd)

PIN:	(~ diode) an acronym formed from "positive-intrinsic-negative" - a semiconductor device consisting of heavily doped p ⁺ and n ⁺ end regions separated by a lightly doped region which can be regarded as intrinsic.
Plasma:	a gas in which a significant fraction of its atoms or molecules are ionized.
Principal Component Analysis:	a statistical procedure for finding a lower-dimensional representation that accounts for the variance among an ensemble of data.
Regression Analysis:	a statistical method concerned with the prediction of one or more variables on the basis of information provided by other measurements or concomitant variables.
Variance:	the weighted average of the squared deviation of the values in a population from the population mean, numerically equal to the square of population's standard deviation.

PURPOSE

The objective of the present Manufacturing Methods and Technology (MM&T) Project is the reduction of microwave semiconductor manufacturing costs through increased product yields. This will be achieved by establishing the correlation between contaminant levels in process materials and their effect upon product yields. These relationships will be used to optimize the manufacturing process toward maximum product yields and minimum unit costs. The project will result in the following developments:

1. An analytical model of the manufacturing process. The model will be implemented in a computer program which will serve as an optimizing control system for the process.
2. A system of batch or lot identification to maintain traceability of contaminants throughout the process, from receiving inspection to the final product.
3. A quantitative chemical analysis system to evaluate contaminants in the materials used in the manufacturing process.
4. A performance specification for an improved manufacturing process control and data management system incorporating these techniques.

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SECTION I

INTRODUCTION

1.1 BACKGROUND

The objective of this program is to improve product yields and consequently lower production costs in the fabrication of microwave semiconductor devices. The yield improvement is predicated on improved control of trace element contamination occurring in process chemicals and reagents. The program will correlate the electrical characteristics of the semiconductor device to measured concentration levels of the elements known to adversely affect the product's performance. The causal relationships between them will then be quantified and employed in a mathematical model of the process. The model in turn will be used to minimize the manufacturing costs of the semiconductor product. A thorough discussion of the project's plans and objectives may be found in the project's First Quarterly Report entitled "MM&T Program to Establish Production Techniques for the Automatic Detection and Quantification of Trace Elements Present in the Production of Microwave Semiconductors," Report Number ECOM 0561-1.

In the manufacture of microwave semiconductor devices, such as high voltage PIN diodes which are used in military electronic systems, the production yields are very low, typically in the order of 5 to 10 percent. These poor yields are attributed in part to the inclusion of trace amounts of contaminants within the crystalline structures of the devices. Contaminating elements in the order of a few parts per billion are often sufficient to degrade, if not destroy, the performance of the device. Currently the military is spending \$28 million annually for devices of this type. Any improvement in production yields is reflected in lower unit costs. At present usage rates, it is expected that this could represent significant cost savings to the military.

Typically, the manufacture of microwave semiconductor devices is accomplished as a series of batch processing steps. For example, ultrapure silicon is procured as a raw material. A quantity of this material is melted and recrystallized into a boule. The boule is entered into stock. Sometime later a boule is drawn from stock and sliced into many wafers. The wafers are ground and polished and returned to stock. Small lots of the wafers are drawn from stock as required. The process continues in this manner through 50 to 60 production steps (refer to flow diagram in Appendix A). Similarly, the reagents used in the various process steps are prepared and dispensed in relatively small batches or lots. A single store of partially processed devices may serve as a source for several different product lines.

Because the manufacture of microwave semiconductors is a batch process, it is difficult to maintain traceability of the end product. If an end item should fail to perform properly because of some intrinsic impurity, it is often impossible to trace the impurity back to its source or point of ingress. However, to control impurity levels to a few parts per billion, it is essential that precise traceability be achieved. Therefore, a fundamental part of the present program must be to devise and implement a system of automatic record keeping and data processing so that yields can be correlated with measurable impurity levels at each step of the process.

Table 1-1 is a partial list of those chemical elements known to adversely affect the performance of microwave semiconductor devices. These impurities may enter interstitially into the crystalline structure of the device, enter on a substitutional basis replacing atoms in the normal crystalline matrix, or react chemically with some of the semiconductor materials. In some cases these elemental impurities may migrate to an interface, inducing effects disproportionate to their average concentrations. In most cases, the effects of these impurities upon the electrical performance of the semiconductor device can be predicted with a high degree of accuracy if one knows the concentration of each. Unfortunately, the concentrations of these elements within the semiconductor material can be measured at only a few points in the manufacturing process. Where tests can be made on the semiconductor material they are generally destructive and analytical data must be gathered on a sampling basis.

TABLE 1-1. CRITICAL CONTAMINANTS

Aluminum	Copper	Molybdenum
Antimony	Fluorine	Nickel
Arsenic	Gallium	Oxygen
Bromine	Germanium	Palladium
Boron	Gold	Phosphorus
Cadmium	Iodine	Potassium
Calcium	Iron	Rubidium
Carbon	Lead	Silver
Cesium	Lithium	Sodium
Chlorine	Magnesium	Tin
Chromium	Manganese	Zinc
Cobalt	Mercury	

The chemical impurities may enter the semiconductor material at any of many points in the manufacturing process. They may be induced from the solvents used for cleaning and etching the crystalline wafers, from the materials used in the formation of epitaxial layers, or from the reagents used in any of the 50 to 60 steps of the manufacturing process.

It must be assumed that all of these contaminants are present to a greater or lesser extent in all of the reagents used in the manufacturing process. However, the semiconductor material is not equally susceptible to contamination at each step of the process. For example, the silicon is susceptible to contamination by oxygen only at elevated temperatures. Therefore, it is not sufficient to only know the concentration of these contaminants in each reagent, but one must also know the transfer ratio associated with each element at each step of the process. That is to say, one must know the quantitative relationship between the level of a contaminant in the reagent and the amount of contamination it can be expected to induce into the semiconductor material. Little is known about these transfer ratios at this time. A major task of the present project is to explicitly define the manufacturing process in terms of the interrelationships between the reagents and the semiconductor material and to

quantify the transfer ratios of pollutants. Once the ratios are established, it remains to set threshold levels consistent with acceptable yields.

Theoretically, one might analyze the chemical composition of the semiconductor material at each step of the manufacturing process, aborting a batch if it is found to be excessively contaminated. Unfortunately such an approach is neither practical nor economical. The semiconductor material is available for testing at only a relatively few points in the manufacturing process, and, where it is available, it is in a solid form which does not readily lend itself to chemical analysis. Further, chemical analyses of elements to a few parts per billion are generally extremely expensive and require highly skilled technicians operating with meticulous care. Thus, the costs associated with such an approach would soon outrun any economic gains which may accrue from improved yield. For these reasons, a fundamental part of this program must be to develop a testing program which is capable of providing the necessary control data within the economic constraints of improved yields.

1.3 THE SPECIFIC PROBLEM

There are uncertainties in processing semiconductor devices in reasonable yields consistently. Controls for times and temperature are known to be quite good. The most significant unknown is the variability of the chemical reagents and deionized water used in wafer fabrication. In addition, although ambient conditions are usually considered to be quite well-controlled with laminar flow, ultrafiltration and frequent particle counts, the chemical nature of airborne contamination is probably the next most significant unknown. The well-known cyclical history of the manufacture of certain microwave semiconductor devices bears these facts out. Frequently, certain devices go out of production; the company is said to have "lost the recipe" temporarily. Then, as mysteriously as the problem arose, its nature being such, the problem disappears; yields return to original levels and production once again returns. The cost to the Government in these situations is significant. Did the problem disappear because a particular lot of reagent material was used up, or replaced?

The problem could have been caused by variability within the manufacturer's specification of some critical contaminant in a reagent, as no quantitative tool is available to monitor on-line each batch for impurity levels and types.

The present project will form the basis for an automatic test and control system, which will include all the appropriate sensors to detect impurity levels in the chemical reagents and particulate matter which might be present in a microwave semiconductor process. This control system will have the capability of analyzing all the chemical inputs to the process: solid, liquid and gaseous. The functions of this detection and control system will be several: to provide warning of excessive contamination as early in the process as possible; to allow contaminated material to be discarded, rather than accrue further manufacturing costs; to be able to identify specifically the critical contaminants to microwave technology, and the threshold levels necessary to precisely control the process; to provide lot traceability throughout the process so that final yields of end products can be correlated with known contamination levels and appropriate yield improvements can be made.

The benefit to the Government and to the microwave industry arising from this project is significant. The keystone of an overall process control and monitoring system is the analytical tool necessary to provide the answers as to what contaminants affect device yields, what are their allowable levels and what steps are to be taken to minimize their effects upon semiconductor yields.

The present project could readily be extended at some future date to include other sensors. Temperature, flow rates, real-time gas stream analysis, pressure, residual atmosphere under high vacuum are all areas which can be readily controlled and monitored by a computerized system. Historical information on the performance of a piece of equipment, comparison with present performance, and trend information are all readily available.

1.4 METHOD OF SOLUTION

The approach to the solution of this problem will be a joint effort between Harris Corporation/PRD Electronics Division, Syosset, New York, acting as prime contractor, and Microwave Associates, Inc., Burlington, Massachusetts, serving as

principal subcontractor. Microwave Associates will provide and operate a standard production facility and process for the manufacture and test of PIN diode chips having specific electrical performance characteristics. An atomic emission spectrometer will be employed as the principal means of chemical analysis. Microwave Associates will monitor the impurity levels of each process chemical as it is used in the production process.

A set of experiments will be designed in which the normal operation of the process is deliberately perturbed to allow evaluation of the effects of impurities upon product yields.

Microwave Associates will gather all pertinent analyses, test data and observations and will transmit them to PRD Electronics on a daily basis. PRD Electronics will analyze these data to evaluate the impact of contamination levels upon the electrical characteristics of the device and upon the product yields.

Material and lot traceability will be meticulously maintained throughout the program to facilitate the accurate correlation of contaminant levels with yields. As correlation is established between contaminant level and yield, a mathematical model of the process will be developed which will provide an independent yield analysis for a particular production run.

Finally, a technical report and demonstration will be developed and presented which will indicate critical process steps, reagents and contaminant levels, the appropriate correlations, the frequency of measurements, and the number and types of sensors needed to control the process to minimize product costs.

1.5 FIRST QUARTER ACTIVITIES

During the first quarter of the program, a computer-controlled spectrometer capable of measuring elements in concentration as low as 20 parts per billion was procured. The instrument will serve as the principal measuring device with which the quality of the chemicals will be monitored. A high voltage PIN diode (e.g., JANTX-1N5710) was selected as the device on which the study would be based and a computer model of its manufacturing process was designed. A technique was developed

for maintaining material and lot traceability throughout the program. All ancillary materials were ordered, facilities were allocated and personnel assigned.

SECTION II

INSTRUMENTATION

2.1 SPECTROMETER INSTALLATION

A plasma emission spectrometer from the Jarrell-Ash Division of Fisher Scientific Company was delivered to Microwave Associates, Burlington, Massachusetts on 29 November 1977. Installation and calibration of the instrument were started on 5 December 1977 and completed on 16 December 1977. The installation and calibration were performed by Jarrell-Ash technicians under the terms of the purchase contract and required approximately 100 man-hours of effort. Dr. George P. Allendorf of Microwave Associates was in attendance throughout the period and received valuable instruction in the operation and maintenance of the instrument. The instrument met or exceeded the performance specifications. The installation was made in the area designated to become an analytical laboratory but delays in the construction of the laboratory were encountered and as of the end of February the laboratory had not been completed. It is not anticipated that the delay will adversely affect the progress of the project.

Upon completion of the installation, practice analyses were performed on a variety of substances including nitric and hydrochloric acids and various water samples. The analyses which were performed were reproducible and the instrument appeared to be stable over an 8-hour period. The main thrust during the remaining weeks of December and early February was to gain familiarity with the instrument. Microwave Associates' personnel developed facility with the operation of the instrument's computer, the loading of programs and the development of matrices.

2.2 SPECTROCHEMICAL MATRICES

In its broadest sense a matrix is something within which something else originates or develops. In geology, for example, it refers to the natural material in which a fossil, metal or crystal is embedded. In chemistry it may be a substance in which a solute or colloid is dispersed. Within the context of the Jarrell-Ash

spectrometer it refers to a format in which a set of computer instructions is developed. Specifically, it refers to the instruction set which the computer is to use in performing the analysis of a prescribed list of chemical elements occurring in a chemical solution.

A spectrometer matrix essentially instructs the computer as to the type of data it is to develop and the format in which it is to be printed. It specifies the spectral line intensities to be measured and the computations it is to make in converting the measured line intensities to concentration levels. The latter requires the input of scaling factors and slope and offset data for each element of interest.

The preparation and calibration of a new matrix is an exacting process requiring careful attention and precise accuracy. It requires a well-planned and meticulously formulated set of standard solution. The adjustment of the slope and offset constants is an interactive process. Using the computer's operating system the matrix is standardized and the primary standards rerun. The measured concentrations are then compared with the stated concentration and corrections applied to obtain improved accuracy. The corrections are edited and the process repeated until the desired accuracy is obtained. The matrix, after some inspection, is then typed manually into the computer. Once in the computer, and corrected in format, a permanent record is made in supplementary memory (disc) and a copy is also made on paper tape.

Typically, with 28 channels to be calibrated the process requires a week or more. By the end of February 1978 the following matrices had been written:

<u>MATRIX NAME</u>	<u>MEDIUM</u>
GAAQ	Aqueous (water)
TRIC	Trichloroethylene
ACET	Acetone
MECL	Methylene Chloride
XYLN	Xylene
ISOP	Isopropyl Alcohol
METH	Methyl Alcohol

An example of one of these matrices is presented as Figure 2-1, GAAQ Matrix Printout, located on page 2-7 with apron to permit viewing while reading the entries in the printout which are interpreted as follows:

Line 1 Command to print a matrix data base (PR).

2-3 Submatrix name, limited to four characters. The first two characters are unique to the particular matrix and the second two identify the submatrix.

4 Number of logic channels, i.e., the number of chemical elements (LCN:28) and the number of submatrices (SM'S:1).

5 Mode, i.e., the type of data to be developed, concentrations (CN). Alternative options include intensities, intensity ratios, and concentration ratios.

6 FORMAT - This line is used to specify the format in which the analytical data are to be printed. The format is limited to five lines. The number of entries per line is to be specified. In this case the computer is instructed (e.g., 1 9 9 9 1) to print one channel on the first line, nine channels each on lines 2, 3 and 4, and one channel on the fifth line. The first channel always is the internal standard. The last channel is number 28 XX, the unused channel.

7-10 Up to four internal standards may be used. Only one was selected and it occupied "physical channel" number 26 (PCN:26). A format priority 1 (PRTY:1) was assigned (see Note 1), as was a preburn of 1 second (PREBRN:1) on an exposure of 10 seconds (EXPOSR:10) (See Notes 2 and 3).

11-15 Five standard solutions were specified (HAR1----HAR5)

17-43 COLUMNSUBJECT

- a Logical Channel Number - order of printout
- b Heading - element symbol
- c Physical Channel Number - the physical location in the spectrometer of the photomultiplier tube for that element
- d Internal Standard Channel Number
- e Location of Bakcgroud Line - not applicable here
- f High Standard - which bottle of solution contains this element
- g Low Standard - the "blank" solution (here #1)
- h Significant Figure Format - number of significant figures to be printed
- i Priority Level - 1 through 7 - can modify printout by specifying priority; instrument will print out priority 2 or 1 automatically (see Note 1)
- j Name of Analytical Curve
- k Background Constant (here 0) to be applied for correction
- l Intensity Ratio of High Standard (10 ppm = 10)
Intensity Ratio is:
$$\frac{\text{Absolute Intensity}}{\text{Internal Standard}}$$
- m Intensity Ratio of Low Standard (blank)
- n Gain - Correction applied to each element after standardization - compensates for instrumental drift; given as G_L in equation (1) below
- p Offset - Correction applied to each element after standardization - coefficient A_L in equation (1)

$$\left(\frac{I_L}{I_S} \right)_o = \left[\begin{array}{c} \left(\frac{I_L}{I_S} \right)_m \\ \hline \left(\frac{I_L}{I_S} \right)_o \end{array} \right] \quad \left(\frac{I_L}{I_S} \right)_m + A_L \quad (1)$$

$$= G_L \left(\frac{I_L}{I_S} \right)_m + A_L$$

where

$\left(\frac{I_L}{I_S} \right)_m$ designates the intensity ratio measured at the time of standardization for the high secondary standard and

$\left(\frac{I_L}{I_S} \right)_o$ represents the intensity ratio for this standard during calibration.

46 Name of the calibration curve used (AQUE)

47 "High" intensity ratio (1000.00) followed by a corresponding "High" concentration (1000.00) (See Note 4.)

48 "Low" intensity ratio (0) followed by "Low" concentration ratio (0)

49-53 Space reserved in computer core memory for future calibration curves, should they be required

55 Submatrix name (AQ for aqueous) and the assigned priority (2)

56-64 Scaling factor for each element in the submatrix (see Note 5). The list of 28 Logic Channel numbers was truncated at 9 to save space in printing

NOTES

1. **PRIORITY:** The AtomComp spectrometer provides several forms in which concentration data can be reported. In the matrix a priority is assigned to each element. Then, at time of analysis, the operator can determine the element concentrations to be printed by specifying a priority level. Elements assigned a priority rating of 1 will always be printed. Elements assigned a priority of 7, the lowest rating, will be printed only when a priority of 7 is specified. An element will be printed only when the priority level specified by the operator is equal to or greater than its assigned rating.

2. **PREBURN:** In some of the antecedents of the Inductively Coupled Argon Plasma AtomComp spectrometer, such as the Direct Current Arc spectrometer, it was necessary to allow time for the sample excitation to stabilize before a meaningful measurement could be made. Provision was made in the computer program to delay any measurement for a specified time to achieve satisfactory operating conditions. The inductively coupled plasma does not require time to stabilize but the software provided with the instrument, being an adaptation of that developed for the earlier instruments, retains this requirement. It is necessary, therefore, to specify a PREBURN time, even though it may be specified as zero.
3. **EXPOSURE:** Exposure time is the interval during which the photomultiplier/integrator circuitry is permitted to respond to the refracted light emanating from the plasma. The period chosen should be long enough to span the expected temporal variations in the intensity of the plasma, but short enough to assure that the high concentration expected will not saturate the integrating or counting circuits.
4. **LINE SEGMENTS:** The AtomComp spectrometer uses a series of straight line segments to represent its "working" or "conversion" curves. The software will accommodate from 1 to 10 line segments per curve. Each line segment is specified by its end points, starting with the highest value and proceeding to the lowest. In the example, GAAQ Matrix Print-out, only one line segment was specified for the intensity ration curve as well as for the concentration curve, each extending from 0 to 1000.00.
5. **SCALING FACTORS:** Scaling factors for each element in the submatrix are accommodated by the AtomComp software. They are particularly useful when testing aliquot diluents or concentrates.

2.3

STANDARDIZATION

After the instrument is turned on and stabilized for several minutes, a standardization procedure is carried out. Standardization involves returning the

PR
 MX NAME:GAAQ
 MX NAME:GA
 # OF LCN'S:28 # OF SM'S: 1
 5 MODE:CN
 FORMAT: 1 9 9 9 1
 IS# 1 PCN:26 PRTY: 1 PREBRN: 1 EXPOSR: 10
 IS# 2
 IS# 3
 10 IS# 4
 STD# 1 HAR1
 STD# 2 HAR2
 STD# 3 HAR3
 STD# 4 HAR4
 15 STD# 5 HAR5

	a	b	c	d	e	f	g	h	i	j	k	l	m	n	p
20	1	LI	40	1	0	3	1	4	1	AQUE	0	10.00	0	1.144	-.037
	2	CU	12	1	0	2	1	4	1	AQUE	0	10.00	0	1.419	-.066
	3	MG	9	1	0	2	1	4	1	AQUE	0	10.00	0	1.694	-.008
	4	CD	5	1	0	2	1	4	1	AQUE	0	10.00	0	2.752	-.129
	5	B	6	1	0	4	1	4	1	AQUE	0	10.00	0	4.363	-.080
	6	GE	49	1	0	4	1	4	3	AQUE	0	10.00	0	1.000	0
	7	P	20	1	0	4	1	4	1	AQUE	0	10.00	0	6.339	-1.11
	8	CR	8	1	0	4	1	4	1	AQUE	0	10.00	0	.8953	-.158
	9	FE	43	1	0	3	1	4	1	AQUE	0	10.00	0	4.546	-.329
	10	NA	41	1	0	3	1	4	1	AQUE	0	10.00	0	4.808	-.165
	11	AG	42	1	0	2	1	4	1	AQUE	0	10.00	0	.2910	-.102
	12	CA	11	1	0	2	1	4	1	AQUE	0	10.00	0	4.351	-.416
	13	HG	44	1	0	5	1	4	1	AQUE	0	10.00	0	5.594	-.808
	14	AL	10	1	0	3	1	4	1	AQUE	0	10.00	0	.6735	-.819
	15	SN	1	1	0	3	1	4	1	AQUE	0	10.00	0	1.279	-.415
	16	AS	2	1	0	4	1	4	1	AQUE	0	10.00	0	2.278	-.448
	17	MO	3	1	0	3	1	4	1	AQUE	0	10.00	0	3.263	-.113
	18	CO	46	1	0	2	1	4	1	AQUE	0	10.00	0	1.439	-.149
	19	K	39	1	0	5	1	4	1	AQUE	0	10.00	0	4.951	-7.07
	20	AU	45	1	0	5	1	4	1	AQUE	0	10.00	0	1.566	-.166
	21	ZN	48	1	0	2	1	4	1	AQUE	0	10.00	0	1.585	-.034
	22	PD	15	1	0	5	1	4	3	AQUE	0	10.00	0	1.000	0
	23	GA	18	1	0	5	1	4	3	AQUE	0	10.00	0	1.000	0
	24	PB	47	1	0	2	1	4	1	AQUE	0	10.00	0	3.643	-.782
	25	SB	4	1	0	3	1	4	3	AQUE	0	10.00	0	1.000	0
	26	MN	7	1	0	2	1	4	1	AQUE	0	10.00	0	.9358	-.021
	27	NI	23	1	0	3	1	4	1	AQUE	0	10.00	0	1.341	-.130
	28	XX	50	1	0	0	0	4	1	AQUE	0	0	0	1.000	0
	45	CURVE NAME :AQUE 1000.00 1000.00 0 0													
	50	CURVE NAME :XXUE CURVE NAME CURVE NAME CURVE NAME CURVE NAME													
	55	SM NAME:AQ PRTY: 2 1 1.000 2 1.000 3 1.000 4 1.000 60 5 1.000 6 1.000 7 1.000 8 1.000 9 1.000													

52-R-76-23

Figure 2-1. GAAQ Matrix Printout

day's intensity ratio points for two different concentrations of each element back to those points obtained during initial calibration, thus reestablishing the original concentration curve. This is a computer function, and results in correction factors referred to as gains and offsets. These new gains and offsets will then remain in effect until the instrument is re-standarized.

An example of the standardization procedure is given below for the matrix GAAQ. The following standard solutions are formulated weekly:

<u>STD</u>	<u>COMPOSITION</u>
HAR-1	Blank
HAR-2	10 ppm of Ag, Ca, Cd, Co, Cu, Mg, Mn, Pb, Zn
HAR-3	10 ppm of Al, Fe, Li, Mo, Na, Ni, Sb, Sn
HAR-4	10 ppm of As, B, Cr, Ge, P
HAR-5	10 ppm of Au, Ga, Hg, Pd, 100 ppm of potassium(K)

Solutions are prepared from stock solutions of Fisher certified standards, 1,000 ppm; aliquot portions are pipetted into chemically cleaned volumetric flasks and the volumes adjusted with D.I. water. Accuracy of solution makeup is known to be better than 1%. Solutions are stored in plastic containers which have been chemically cleaned ("Triton - X - 100, a low metallic content detergent, followed by aqua regia treatment, followed by deionized water rinses"). Shelf time of 1 to 10 ppm standards is generally low: 1 to 2 days for 1 ppm; 1 week for 10 ppm. Precipitation, leaching and absorption are some of the mechanistic reasons for standard concentrations changing.

The actual standardization process is then performed, and the output data for each standard is shown below. Note that the units are absolute intensities and *not* concentrations. Also note the antimony (Sb) channel had malfunctioned and three channels, Ga, Pd and Ge, were not standardized on this run (due to unavailability of these standards). The printout of gains and offsets based on a standardization run is shown in Figure 2-2. For comparison, gains and offsets from the previous days are shown in Figure 2-3. Generally, the numbers should be within 20% of one another from day to day; large variations of fluctuations signal problems. Procedures are then available to reestablish proper operating conditions. The standardization

*EGIGIGIGIAIN/HARI

(SEE NOTE 1)

E

G

HAR-1 - BLANK

BURN # 1 GAAQ 11:42 18FEB78

I

IS

4012

	CU	MG	CD	B	GE	P	CR	FE
LI	295	29	358	110	4277	982	1177	469
170								
NA	AG	CA	HG	AL	SN	AS	MO	CO
217	2341	618	904	6118	1511	1194	221	692
K	AU	ZN	PD	GA	PB	SB	MN	NI
8922	722	145	9158	3325	1349	2030	146	614
XX								
9								

(SEE NOTE 2)

G

BURN # 2 GAAQ 11:43 18FEB78

I

IS

4013

	CU	MG	CD	B	GE	P	CR	FE
LI	288	29	357	109	4173	950	1146	458
166								
NA	AG	CA	HG	AL	SN	AS	MO	CO
213	2300	606	875	6075	1473	1174	219	677
K	AU	ZN	PD	GA	PB	SB	MN	NI
8729	710	138	8906	3250	1298	2022	142	590
XX								
8								

(SEE NOTE 3)

G

BURN # 3 GAAQ 11:44 18FEB78

I

IS

4013

	CU	MG	CD	B	GE	P	CR	FE
LI	285	28	346	107	4022	925	1134	456
167								
NA	AG	CA	HG	AL	SN	AS	MO	CO
212	2272	596	874	6000	1469	1118	215	672
K	AU	ZN	PD	GA	PB	SB	MN	NI
8674	698	137	8795	3207	1305	2214	138	605
XX								
12								

NOTES:

1. PERTINENT COMPUTER COMMANDS
 - * STAND BY TO RECEIVE INSTRUCTIONS
 - E ERASE DATA IN BURN BUFFERS
 - G GO, BURN A SAMPLE
 - I PRINT ABSOLUTE INTENSITIES
 - A AVERAGE DATA IN BURN BUFFERS
 - N AVERAGE STANDARDIZATION BURNS AND REQUEST NAME OF SAMPLE
 - / DESIGNATES THAT WHICH FOLLOWS TO BE COMMENTARY, NOT TO BE INTERPRETED AS A COMMAND.
2. IS: THE INTENSITY OF THE INTERNAL STANDARD IS ALWAYS PRINTED. IT HAS A PRIORITY OF 1.
3. THE ATOMCOMP SPECTROMETER PROVIDES A SPECIAL EXIT SLIT FOR USE WITH AN EXTERNAL REFRACTOMETER. THE CHANNEL NORMALLY IS UNCALIBRATED. ITS POSITION IS DICTATED BY MOUNTING CONSIDERATIONS RATHER THAN BY ANY CONSTRAINT TO INTERCEPT A USEFUL SPECTRAL LINE. IN THE PRESENT APPLICATION THE CHANNEL WAS LABELED XX, ALTHOUGH IT WAS NOT USED. THE MEASURED INTENSITIES ARE WITHOUT MEANING IN AS MUCH AS THE CHANNEL WAS NOT CALIBRATED. ITS PRINTOUT COULD HAVE BEEN SUPPRESSED HAD IT BEEN ASSIGNED A PRIORITY OF "7" RATHER THAN "1".

G

BURN # 4 GAAQ 11:44 18FEB78

I

IS

4014

	CU	MG	CD	B	GE	P	CR	FE
LI	294	29	353	102	4159	967	1179	468
173								
NA	AG	CA	HG	AL	SN	AS	MO	CO
220	2342	621	905	6160	1457	1164	221	690
K	AU	ZN	PD	GA	PB	SB	MN	NI
8836	726	140	9139	3319	1312	1987	146	628
XX								
8								

A

AVERAGE GAAQ 11:45 18FEB78

I

IS

4013

	CU	MG	CD	B	GE	P	CR	FE
LI	290	29	353	109	4158	956	1159	463
169								
NA	AG	CA	HG	AL	SN	AS	MO	CO
215	2314	610	889	6088	1477	1162	219	683
K	AU	ZN	PD	GA	PB	SB	MN	NI
8790	714	140	8999	3275	1316	2063	143	609
XX								
9								

N

ENTER STD ID HARI

52-R-76-24

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 1 of 5)

EGIGIGIGIAIN/HAR2

E

G

HAR-2

BURN # 1 GAAQ 11:46 18FEB78

I

IS

4013

LI	CU	MG	CD	B	GE	P	CR	FE
169	27739	32174	28252	118	4208	1177	1253	532
NA	AG	CA	HG	AL	SN	AS	MO	CO
245	164790	14041	1273	6456	1535	1206	232	40104
K	AU	ZN	PD	GA	PB	SB	MN	NI
8668	1127	37489	9116	3234	15830	2449	56630	756
XX								

8

G

BURN # 2 GAAQ 11:47 18FEB78

I

IS

4014

LI	CU	MG	CD	B	GE	P	CR	FE
170	27369	31960	28307	119	4268	1129	1280	542
NA	AG	CA	HG	AL	SN	AS	MO	CO
250	162958	13963	1285	6495	1501	1253	234	39810
K	AU	ZN	PD	GA	PB	SB	MN	NI
8825	1141	37270	9253	3322	15708	2396	56152	757
XX								

9

G

BURN # 3 GAAQ 11:47 18FEB78

I

IS

4014

LI	CU	MG	CD	B	GE	P	CR	FE
166	27486	31478	27796	114	4193	1140	1230	522
NA	AG	CA	HG	AL	SN	AS	MO	CO
237	162597	13710	1250	6366	1483	1201	229	39361
K	AU	ZN	PD	GA	PB	SB	MN	NI
8607	1111	36670	8879	3219	15609	2303	55432	729
XX								

9

G

BURN # 4 GAAQ 11:48 18FEB78

I

IS

4013

LI	CU	MG	CD	B	GE	P	CR	FE
169	28014	32240	28575	117	4242	1163	1252	534
NA	AG	CA	HG	AL	SN	AS	MO	CO
238	165159	14078	1266	6504	1521	1220	230	40256
K	AU	ZN	PD	GA	PB	SB	MN	NI
8659	1137	37574	8978	3247	15835	2357	56738	740
XX								

8

A

AVERAGE GAAQ 11:48 18FEB78

I

IS

4013

LI	CU	MG	CD	B	GE	P	CR	FE
168	27652	31963	28232	117	4228	1152	1254	532
NA	AG	CA	HG	AL	SN	AS	MO	CO
242	163876	13948	1268	6455	1510	1220	231	39883
K	AU	ZN	PD	GA	PB	SB	MN	NI
8690	1129	37250	9056	3255	15745	2376	56238	745
XX								

8

N

ENTER STD ID HAR2

82-W-76-28

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 2 of 5)

EGIGIGIGIAACN/HAR3

E

G

HAR-3

BURN # 1 GAAQ 11:51 18FEB78

I

	IS									
	4011	LI	CU	MG	CD	B	GE	P	CR	FE
22035	505			62	407	138	4600	1046	1246	11139
NA	AG	CA	HG	AL		SN	AS	MO	CO	
5934	2546			692	1115	61324	23015	1671	13575	861
K	AU	ZN	PD	GA		PB	SB	MN	NI	
8947	762			358	9333	3392	1465	11183	342	37177
XX										
9										

G

BURN # 2 GAAQ 11:52 18FEB78

I

	IS									
	4011	LI	CU	MG	CD	B	GE	P	CR	FE
24361	458			60	396	138	4508	1050	1204	11153
NA	AG	CA	HG	AL		SN	AS	MO	CO	
6573	2466			674	1082	62805	23181	1626	13748	828
K	AU	ZN	PD	GA		PB	SB	MN	NI	
8727	746			345	8997	3288	1458	13321	334	37371
XX										
9										

G

BURN # 3 GAAQ 11:53 18FEB79

I

	IS									
	4013	LI	CU	MG	CD	B	GE	P	CR	FE
22902	433			58	405	137	4594	1047	1208	11092
NA	AG	CA	HG	AL		SN	AS	MO	CO	
6137	2482			674	1084	61763	23132	1638	13657	829
K	AU	ZN	PD	GA		PB	SB	MN	NI	
8811	749			338	9084	3312	1452	14731	330	37119
XX										
9										

G

BURN # 4 GAAQ 11:53 18FEB78

I

	IS									
	4013	LI	CU	MG	CD	B	GE	P	CR	FE
22582	438			58	1042	149	4840	1092	1269	11159
NA	AG	CA	HG	AL		SN	AS	MO	CO	
6097	2547			701	1130	61751	25521	2274	13919	901
K	AU	ZN	PD	GA		PB	SB	MN	MI	
9065	772			800	9452	3420	1617	*	337	37420
XX										
10										

A

AVERAGE GAAQ 11:54 18FEB78

I

	IS									
	4012	LI	CU	MG	CD	B	GE	P	CR	FE
22970	458			60	562	140	4635	1059	1232	11133
NA	AG	CA	HG	AL		SN	AS	MO	CO	
6185	2510			685	1103	61911	23712	1802	13725	855
K	AU	ZN	PD	GA		PB	SB	MN	NI	
8887	757			460	9216	3353	1498	624053	336	37271
XX										
9										

A

88-8-78-26

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 3 of 5)

EGIGIGIGIAIACN/HAR4

E
G

HAR-4

BURN # 1 GAAQ 11:57 18FEB78
I

	IS								
4010	LI	CU	MG	CD	B	GE	P	CR	FE
	193	338	37	384	10087	4557	9394	60247	1622
	NA	AG	CA	HG	AL	SN	AS	MO	CO
4319	2514	670	981	6413	1619	24195	281		795
K	AU	ZN	PD	GA	PB	SB	MN	NI	
12437	757	429	9470	3469	1401	3704	178		720
	XX								
	9								

G

BURN # 2 GAAQ 11:58 18FEB78
I

	IS								
4012	LI	CU	MG	CD	B	GE	P	CR	FE
	189	343	37	389	10274	4697	9589	61422	1642
	NA	AG	CA	HG	AL	SN	AS	MO	CO
4429	2570	680	998	6515	1633	24754	277		816
K	AU	ZN	PD	GA	PB	SB	MN	NI	
12726	778	439	9678	3527	1449	3229	182		711
	XX								
	9								

G

BURN # 3 GAAQ 11:58 18FEB78
I

	IS								
4011	LI	CU	MG	CD	B	GE	P	CR	FE
	180	337	36	381	10360	4438	9668	61575	1638
	NA	AG	CA	HG	AL	SN	AS	MO	CO
4606	2470	660	970	6457	1616	24719	263		808
K	AU	ZN	PD	GA	PB	SB	MN	NI	
12688	758	436	9330	3417	1402	2989	176		678
	XX								
	9								

G

BURN # 4 GAAQ 11:59 18FEB78
I

	IS								
4012	LI	CU	MG	CD	B	GE	P	CR	FE
	184	340	37	385	10421	4714	9665	62210	1650
	NA	AG	CA	HG	AL	SN	AS	MO	CO
4374	2536	677	987	6447	1633	25087	262		806
K	AU	ZN	PD	GA	PB	SB	MN	NI	
12685	781	444	9995	3517	1469	2823	180		704
	XX								
	9								

A

AVERAGE GAAQ 11:59 18FEB78
I

	IS								
4011	LI	CU	MG	CD	B	GE	P	CR	FE
	186	339	37	385	10285	4601	9579	61363	1638
	NA	AG	CA	HG	AL	SN	AS	MO	CO
4432	2522	672	984	6458	1625	24689	271		806
K	AU	ZN	PD	GA	PB	SB	MN	NI	
12634	768	437	9618	3483	1430	3186	179		703
	XX								
	9								

N

ENTER STD ID HAR4

82-R-76-27

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 4 of 5)

EGIGIGIGIAIN/HARS

E

G

HAR-5

BURN # 1 GAAQ 12:01 18FEB78

I

IS

4011

LI	CU	MG	CD	B	GE	P	CR	FE
158	314	30	310	124	3887	872	1104	423
NA	CA	CA	HG	AL	SN	AS	MO	CO
217	2803	563	7694	5755	1401	1159	203	612
K	AU	ZN	PD	GA	PB	SB	MN	NI
58365	27853	130	7903	2946	1165	2199	130	554
XX								
12								

G

BURN # 2 GAAQ 12:02 18FEB78

I

IS

4011

LI	CU	MG	CD	B	GE	P	CR	FE
161	320	31	318	121	3868	846	1098	416
NA	AG	CA	HG	AL	SN	AS	MO	CO
218	2630	569	7821	5816	1400	1144	205	626
K	AU	ZN	PD	GA	PB	SB	MN	NI
58878	28433	130	7992	2968	1157	2118	130	565
XX								
12								

G

BURN # 3 GAAQ 12:02 18FEB78

I

IS

4006

LI	CU	MG	CD	B	GE	P	CR	FE
160	323	30	324	121	3901	921	1118	425
NA	AG	CA	HG	AL	SN	AS	MO	CO
220	2560	580	7800	5755	1417	1173	208	634
K	AU	ZN	PD	GA	PB	SB	MN	NI
56490	28371	132	8159	3039	1217	2207	133	580
XX								
12								

G

BURN # 4 GAAQ 12:03 18FEB78

I

IS

4009

LI	CU	MG	CD	B	GE	P	CR	FE
160	326	32	331	118	4026	894	1110	432
NA	AG	CA	HG	AL	SN	AS	MO	CO
220	2476	580	8060	5922	1457	1169	205	633
K	AU	ZN	PD	GA	PB	SB	MN	NI
61651	29123	132	8134	3026	1216	2026	134	550
XX								
12								

A

AVERAGE GAAQ 12:04 18FEB78

I

IS

4009

LI	CU	MG	CD	B	GE	P	CR	FE
160	321	31	321	121	3920	883	1107	424
NA	AG	CA	HG	AL	SN	AS	MO	CO
219	2617	573	7844	5812	1419	1161	205	626
K	AU	ZN	PD	GA	PB	SB	MN	NI
58846	28445	131	8047	2995	1189	2137	132	562
XX								
12								

N

ENTER STD ID HARS

Figure 2-2. Standardization Runs, Standards 1-5 (Sheet 5 of 5)

52-R-76-28

*W
W

GAINS GAAQ 10:09 23FEB78

IS

0

	LI	CU	MG	CD	B	GE	P	CR	FE
.9296	1.371	1.280	2.254	3.760	-2881	6.168	.7537	3.758	
NA	AG	CA	HG	AL	SN	AS	MO	CO	
4.000	.2557	3.214	5.169	.6044	.9132	2.156	2.646	.8525	
K	AU	ZN	PD	GA	PB	SB	MN	NI	
22.47	1.468	1.268	-3442	-5882	4.889	53881	.6867	1.093	
XX									
1.000									

OFFSETS GAAQ 10:10 23FEB78

IS

0

	LI	CU	MG	CD	B	GE	P	CR	FE
-.0310	-.0695	-.0078	-.1226	-.0793	2881	-1.257	-.1546	-.3056	
NA	AG	CA	HG	AL	SN	AS	MO	CO	
-.1450	-.0987	-.3383	-.7789	-.6752	-.2981	-.4614	-.0942	-.1339	
K	AU	ZN	PD	GA	PB	SB	MN	NI	
-34.54	-.1729	-.0274	1082	3242	-.6336	1062	-.0175	-.1119	
XX									
0									

*†W
†W

*

W

GAINS CAAQ 14:21 22FEB78

IS

0

	LI	CU	MG	CD	B	GE	P	CR	FE
.8561	1.247	1.330	1.342	4.752	-3881	6.904	.9486	4.662	
NA	AG	CA	HG	AL	SN	AS	MO	CO	
3.564	.2550	3.351	5.648	.6485	1.098	2.588	2.959	.7798	
K	AU	ZN	PD	GA	PB	SB	MN	NI	
24.59	1.478	1.276	-19.06	-57.72	3.591	0.0001	.7554	1.337	
XX									
1.000									

OFFSETS GAAQ 14:22 22FEB78

IS

0

	LI	CU	MG	CD	B	GE	P	CR	FE
-.0238	-.0701	-.0085	-.2734	-.1028	28.91	-1.241	-.2125	-.4145	
NA	AG	CA	HG	AL	SN	AS	MO	CO	
-.1395	-.1070	-.3783	-.9467	-.8240	-.4627	-.6924	-.1375	-.1365	
K	AU	ZN	PD	GA	PB	SB	MN	NI	
-41.31	-.2006	-.0575	32.85	34.85	-.7977	10801	-.0202	-.1473	
XX									
0									

*

NOTE 1. COMPUTER INSTRUCTIONS

* STAND BY TO RECEIVE INSTRUCTIONS.

W WRITE CURRENT GAINS AND OFFSETS.

IW WRITE CURRENT MATRIX ON SUPPLEMENTARY
MEMORY.

NOTE 2. THE ANTIMONY (Sb) CHANNEL MALFUNCTIONED AND THE
THREE CHANNELS, GALLIUM (Ga), PALLADIUM (Pd) AND
GERMANIUM (Ge), WERE NOT STANDARDIZED ON THIS RUN.
BECAUSE AT THE TIME CHEMICAL STANDARDS WERE NOT
AVAILABLE FOR THOSE ELEMENTS, THE MEANINGLESS
RECORDS WERE MANUALLY X-ED OUT.

Figure 2-3. Gains and Offsets, 23 and 22 February 1978 Runs
82-R-76-29

can then be checked by rerunning any of the standards, or a solution made up to be of some intermediate concentration of elements (e.g., 5 ppm). In our experience to date, accuracy of this procedure has been impressive.

2.4 LIMITS OF DETECTABILITY

Included in the software provided is a statistical program which allows a sequence of up to 10 burns to be performed and which then calculates the average, the standard deviation, and the relative standard deviation. By definition, the limits of detectability are twice the standard deviation of the blank. An example of a statistical run on a blank solution is included (Figure 2-4). Note that the standard deviations in most cases push the limit of detectability to the low parts per billion range. Also included are the average, standard deviation and relative standard deviation for a statistical run of one of the standards (Figure 2-5); note that the relative standard deviation for the elements of interest are all better than 1%. The units recorded in this statistical presentation are concentrations in parts per million (ppm).

2.5 ANALYSIS OF ORGANIC MATERIALS

A variety of problems was encountered in the analysis of organic media. First, while chemical standards in aqueous solutions were readily available from several chemical supply houses, standards in organic solutions were not. After much searching, standards were obtained from a division of Continental Oil Company. These standards were formulated as typically 500 to 900 ppm of the metallic elements in a hydrocarbon oil. These standards were used as aliquots and diluted in the appropriate organic base, without the need for solubilizers. Second, when running organics, molecular carbon was deposited on the inner surfaces of the plasma torch. The carbon absorbed the infrared radiation causing the glass of the torch to overheat. The torch was designed to provide a protective shield of argon gas around the plasma. This served to cool the glass and to flush the molecular carbon away. It was found that by careful adjustment of the gas flow, the rate of carbon accumulation could be greatly reduced but not totally eliminated. As a result, when organic materials were analyzed, the torch required frequent cleaning and adjusting. The gas flow was controlled by means of an uncalibrated pressure control valve. An indicated pressure of

WC
 BURN NO.0 GAAQ 11:03 23FEB78 (SEE NOTE 1)
 IS
 3988
 LI CU MG CD B GE P CR FE
 .0115 .0147 .0028 .0164 .0093 0 0 .0300 .0647
 NA AG CA HG AL SN AS MO CO
 .0315 .0203 .0647 .1556 .0810 .0694 .0647 .0557 .0313
 K AU ZN PD GA PB SB MN NI
 6.472 .0384 .0073 0 0 .2172 .1394 .0030 .0245
 XX
 .0023

BURN NO.1 GAAQ 11:04 23FEB78 (SEE NOTE 2)
 3987
 .0094 .0130 .0025 .0114 .0034 0 .0259 .0270 .0563
 .0316 .0173 .0551 .1247 .0678 .0438 .0751 .0398 .0282
 5.980 .0311 .0060 0 0 .2015 .1663 .0028 .0259
 .0023

BURN NO.2 GAAQ 11:05 23FEB78
 3987
 .0034 .0137 .0028 .0142 .0112 0 0 .0303 .0620
 .0326 .0201 .0656 .1506 .0584 .0486 .0756 .0345 .0273
 6.414 .0359 .0060 0 0 .2591 .1663 .0032 .0210
 .0023

BURN NO.3 GAAQ 11:06 23FEB78
 3988
 .0082 .0130 .0025 .0136 .0093 0 .0163 .0274 .0623
 .0335 .0187 .0615 .1387 .0510 .0472 .0533 .0311 .0303
 6.382 .0336 .0060 0 0 .02246 .1394 .0028 .0196
 .0023

BURN NO.4 GAAQ 11:07 23FEB78
 3987
 .0075 .0144 .0023 .0181 .0093 0 0 .0316 .0582
 .0296 .0201 .0648 .1506 .0782 .0408 .0762 .0292 .0307
 5.918 .0352 .0063 0 0 .2248 .1663 .0032 .0246
 .0025

BURN NO.5 GAAQ 11:07 23FEB78
 3987
 .0075 .0137 .0025 .0142 .0093 0 0 .0312 .0563
 .0346 .0195 .0616 .1455 .0641 .0285 .0788 .0252 .0282
 6.674 .0370 .0060 0 0 .2444 .1663 .0038 .0196
 .0023

BURN NO.6 GAAQ 11:08 23FEB78
 3987
 .0068 .0134 .0025 .0142 .0093 0 0 .0304 .0544
 .0296 .0198 .0632 .1390 .0656 .0310 .0583 .0232 .0290
 6.414 .0341 .0057 0 0 .2505 .1663 .0030 .0232
 .0023

NOTE 1. WC IS A COMPUTER INSTRUCTION WHICH WHEN USED WITH THE ATOMCOMP STATISTICAL PACKAGE COMMANDS THE SYSTEM TO MAKE 10 BURNS AND TO PRINT THE AVERAGE CONCENTRATIONS.

NOTE 2. THE SPECTROMETER IS TIME CONSTRAINED BY ITS ASSOCIATED PRINTER, I.E., IT TAKES MUCH LONGER TO PRINT THE RESULTS OF AN ANALYSIS THAN IT DOES TO COMPLETE THE ANALYSIS. TO SAVE TIME, HEADINGS AND LABELS ARE CUSTOMARILY OMITTED WHENEVER THE MEANING OF THE DATA IS NOT OBSCURED BY DOING SO.

52-R-76-30 Figure 2-4. Statistical Package, Blank Solution (Sheet 1 of 2)

BURN NO.7 GAAQ 11:09 23FEB78

3987
.0068 .0151 .0028 .0198 .0121 0 0 .0354 .0648
.0356 .0224 .0737 .1766 .0630 .0619 .0783 .0259 .0303
7.643 .0407 .0060 0 0 .2346 .1663 .0035 .0221
.0023

BURN NO.8 GAAQ 11:10 23FEB78

3987
.0075 .0154 .0028 .0164 .0121 0 .0105 .0369 .0714
.0336 .0227 .0761 .1882 .0744 .0530 .0643 .0232 .0365
7.203 .0410 .0063 0 0 .2260 .1663 .0035 .0265
.0025

BURN NO.9 GAAQ 11:10 23FEB78

3987
.0066 .0147 .0025 .0153 .0121 0 0 .0354 .0582
.0356 .0224 .0721 .1675 .0795 .0931 .0491 .0225 .0314
7.079 .0407 .0063 0 0 .2689 .1663 .0035 .0246
.0023

AVERAGE

IS
3987
LI CU MG CD B GE P CR FE
.0080 .0141 .0027 .0154 .0183 0 .0053 .0316 .0609
NA AG CA HG AL SN AS MO CO
.0328 .0200 .0658 .1537 .0683 .0517 .0673 .0318 .0303
K AU ZN PD GA PB SB MN NI
6.618 .0368 .0062 0 0 .2352 .1609 .0032 .0232
XX
.0028

STANDARD DEVIATION

IS
U
LI CU MG CD B GE P CR FE
.0015 .0009 .0002 .0024 .0015 0 .0093 .0033 .0052
NA AG CA HG AL SN AS MO CO
.0022 .0017 .0064 .0191 .0098 .0192 .0109 .0103 .0026
K AU ZN PD GA PB SB MN NI
.5441 .0034 .0004 0 0 .0205 .0113 .0003 .0025
XX
.0001

* RELATIVE STANDARD DEVIATION

IS
U
LI CU MG CD B GE P CR FE
18.44 6.178 6.360 15.85 14.40 0 175.5 10.51 8.531
NA AG CA HG AL SN AS MO CO
6.740 8.548 9.689 12.41 14.41 37.06 16.23 33.20 8.558
K AU ZN PD GA PB SB MN NI
8.221 9.259 6.897 0 0 8.733 7.037 8.656 10.72
XX
4.590

52-8-76-31

Figure 2-4. Statistical Package, Blank Solution (Sheet 2 of 2)

AVERAGE

IS

3876

	AG	AL	AS	AU	B	CA	CD	CO	CR	CU
10.08	.6017	.0281	.1181	.0008	10.01	9.752	9.972	.0296	10.09	
FE	GA	GE	HG	K	LI	MG	MN	MO	NA	
.1214	-.0155	.2251	.3653	-1.753	-.0004	10.02	9.723	.0026	-1.407	
NI	P	PB	PD	SB	SN	ZN				
.0264	-.1591	10.04	.0108	.0349	-.0329	10.02				

STANDARD DEVIATION

IS

U

	AG	AL	AS	AU	B	CA	CD	CO	CR	CU
.0603	.0262	.0045	.0019	.0010	.0744	.0441	.0574	.0011	.0427	
FE	GA	GE	GH	K	LI	MG	MN	MO	NA	
.0079	.0059	.1269	.0092	.1363	.0007	.0497	.0486	.0012	.0067	
NI	P	PB	PD	SB	SN	ZN				
.0024	.0303	.0685	.0163	.0078	.0104	.0322				

% RELATIVE STANDARD DEVIATION

IS

U

	AG	AL	AS	AU	B	CA	CD	CO	CR	CU
.5986	4.360	15.89	1.648	124.0	.7430	.4522	.5751	3.606	.4235	
FE	GA	GE	HG	K	LI	MG	MN	MO	NA	
6.527	-37.90	56.38	2.515	-7.776	-176.7	.4963	.4996	45.31	-.4781	
NI	P	PB	PD	SB	SN	ZN				
9.185	-19.07	.6816	150.1	22.46	-31.50	.3211				

%

52-8-76-32

Figure 2-5. Statistical Data, Standard No. 2

2 Kg/sq. cm. (28.5 psi) was found to be satisfactory. Excessive flow rates were found to make the plasma unstable or to extinguish it. Insufficient flow allowed carbon to rapidly accumulate.

A third problem was concerned with attaining a constant aspiration rate for the sample. The organic solvents of interest generally are highly volatile. When these materials were introduced into the aspirator, the aspiration rate was found to be unstable and quenched the plasma torch. In the Jarrell-Ash spectrometer, the sample was normally drawn through a capillary tube by a negative pressure created by the Venturi effect of the aspirator. The aspiration rate was controlled by regulating the pressure of the argon gas fed to the Venturi jet. For samples which had high vapor pressures the rapid reduction of pressure in the immediate vicinity of the Venturi tended to vaporize rather than atomize the material, thus resulting in erratic pressure variations. The operator was constantly striking a balance between the loss of aspiration and blowing out the flame with a burst of material. One solution was to introduce the sample material under positive rather than negative pressure. This could be accomplished by using a positive displacement pump to inject the material at a precisely controlled rate. To minimize any pulsation in the flow which might be induced by the pumping action, a peristaltic type pump was selected.

A fourth problem in analyzing organics was concerned with the intense green color observed at the base of the plasma torch. Upon investigation it was found to be the product of molecular carbon species. To minimize possible interference from those bands, it was found that the plasma torch had to be precisely positioned to assure that the region of maximum atomic emission was scanned. The intense green color suggested that its principal energy bands were between 5250 \AA and 5750 \AA and fortunately the spectrometer, as configured for this application, did not monitor any line between 4632 \AA (Ni) and 5890 \AA (Na). Furthermore, second order dispersion of the green would fall (above 10,500 \AA) in the far infrared, beyond the range of the spectrometer's optical system and beyond 7664 \AA (K), the highest line which was monitored. However, carbon, which is a major constituent of all organics, exhibits a strong line at 1930 \AA just 6 \AA from the 1936 \AA line of arsenic, a trace element of interest. For any element whose emission is 2500 \AA or less, corrections must be

made for emissions from such molecular products as C=N, C=C and O=H. This would include nearly half of the 27 trace elements of interest. To help resolve these interferences, the elements which are to be analyzed and the appropriate wavelengths under investigation were identified to scientists at the Analytical Chemistry Laboratory at Watertown Arsenal. They will identify the possible interferences. Where interferences exist, quantitative techniques are available for automatically correcting the data in the computer to improve the accuracy of the analysis.

2.6 SPECTRUM SHIFTER

The project will determine quantitatively what levels of impurities in process chemicals affect device performance. From what is known at this time, it would appear that meaningful data must be obtained on concentrations in the parts-per-billion range. These levels approach the limit of detection for the spectrometer. At such concentration levels the background emission intensity at a given exit slit may be more than 50 to 75% of the total intensity falling upon the photomultiplier tube. In making accurate measurements in the parts-per-billion range, it is necessary to compensate for the background emission falling on each exit slit, as well as for any slow instrumentation drift. This is accomplished by frequently standardizing the instrument against standard solutions having compositions closely approximating those of the sample under test. This technique is very exacting and time-consuming. It works well in compensating for slow instrumentation drifts and for changes in background levels which are proportional to the line intensity or to the intensity of the internal standard. It presupposes however that the chemical and physical characteristics of the sample are comparable to those of the standard. If, for any of a variety of reasons, e.g., a sample of different viscosity, the background intensity varies independently of the signal, a significant error may be introduced. A more effective method would be to measure the background at each exit slit each time the line intensity (i.e., line plus background) is measured.

Jarrell-Ash presently manufactures a device which automatically corrects for background illumination at each exit slit each time a measurement is made. It dynamically rotates the spectral array through a very small angle so that the photomultiplier tube senses first the intensity of the spectral line plus the background and

then the spectral array shifts and the photomultiplier senses only the background intensity immediately adjacent to the line. The device consists of a small (approximately 3 mm thick) glass plate inserted in the polychromic light beam immediately behind the entrance slit. The plate is rotated about a vertical axis, normal to the optical plane. The plate, driven by an electrical stepping motor, alternately assumes one of two angular positions, shifting the spectrum a few angstroms from right to left and back again. This permits alternately making a set of measurements at the peak of each line response followed immediately by a similar set offset from the peak by a fixed amount. The computer compares the value of intensity at the peak of each line to the measured value of background interference immediately adjacent to each line rather than to some assumed (standardized) level. The device dramatically improves the accuracy of the spectrometer at low concentration levels.

A spectrum shifter of this type was purchased from Jarrell-Ash and was scheduled for delivery and installation on 4 April 1978.

2.7 ANCILLARY EQUIPMENT

Standards for all elements of interest (except palladium) were received, and standard solutions are being prepared weekly.

All chemical glassware was received for accurate standard solution preparation as were all sampling vials, syringes and labels.

2.8 TRAINING

During the installation of the spectrometer at Microwave Associates, service engineers from Jarrell-Ash provided training in many aspects of the instrument, including sample preparation, matrix construction, operation, troubleshooting, and preventive maintenance. As an extension of that training, three people attended a 1-week intensive course of study at the facilities of Jarrell-Ash Division, Waltham, Massachusetts. The formal training course emphasized spectrochemical theory and refinements in analytical technique. As a consequence of the formal training, and of the experience accrued from almost constant operation of the instrument from the time of its installation, the analytic skills required for the project were developed.

SECTION III

DATA PROCESSING

3.1 DATA TRANSMISSION

The project plan called for Microwave Associates to analyze each of the process chemicals and to measure the product's electrical characteristics. These data were to be transmitted to PRD Electronics, where they would be analyzed in the UNIVAC 1108 computer facility.

An unexpected technical problem arose with regard to transmitting the spectrometer's analytical data from Burlington, Massachusetts, to Syosset, New York. It was originally planned to store the data on the unused magnetic disc (Floppy Disk) in the spectrometer and periodically transmitting it, via the PDP-8A computer in the spectrometer and a modem, over telephone lines to Syosset. This was to be accomplished by making a minor modification to the Jarrell-Ash software to permit writing and reading a file on the unused disc. In attempting to implement the plan, it was discovered that the Jarrell-Ash software was written in assembly language, was poorly documented without annotation, and was considered by Jarrell-Ash to be proprietary. Were Jarrell-Ash to write the software modification, it would need to be done by the original authors at Jarrell-Ash who were currently dedicated to a company program which precluded their being available for a minimum of 6 months. Were PRD to write the new software it would require several months to decipher the undocumented coding. A tentative solution was adopted which consisted of leasing a small cassette recorder. The data was to be written on the magnetic tape as it was printed on the LA-36 Decwriter and subsequently transmitted via modem over a telephone line to Syosset.

The particular cassette recorder chosen was a Techtran 815 Data-cassette manufactured by Techtran Industries, Inc., Rochester, New York. The device was leased from Computrend, Inc., Burlington, Massachusetts, which also provided a maintenance and service contract to support its operation.

The operating features and general specification of the device were as follows:

Capacity per cassette:

145,000 characters

Media:

Phillips-type cassette

Coding:

ASCII, 8-level

Transmission:

Half/Full Duplex

Speeds:

110/300 baud switch selectable

Interfaces:

Terminal-RS 232C/CCITT/20 ma
Modem/CPU-RS-232C/CCITT

Operating modes:

Read, Write, Fast Forward

Remote control:

Read, Write, Rewind, Fast Forward, Edit

Source control:

Automatic

Data edit:

Character delete

CR delay:

Fixed; 360 ms

Size:

5 x 7 1/4 x 11 Inches

Weight:

6 lbs.

Power:

115 VAC 60 Hz (100/230 V, 50 Hz optional)

To correct transmission errors, the PDP-8 computer in the spectrometer was programmed to read out all significant analytical data, i.e., average concentrations, wafer identification and station names, in triplicate. These data, together with appropriate heading and operator commentary, were recorded on the tape cassette. Upon reception at PRD Electronics, the significant data were corrected for transmission errors prior to their being entered into the data base file. Insofar as could be determined by trial runs, the data transmission system worked satisfactorily.

3.2 DATA BASE FILE

As they are received at PRD Electronics, the analytical data are checked for errors. The transmission errors are corrected and the corrected data filed on a FASTRAND disc. Subsequently, these data are recorded in a permanent backup file on magnetic tape. The data from the FASTRAND are stripped of all superfluous legends and mnemonic symbols and entered into a data base file. Periodically the unprocessed data are transcribed on magnetic tape as a permanent record and purged from the FASTRAND disc.

Two types of data base files were designed. The first was configured under the control of a UNIVAC DMS 1100 (FORTRAN) data management system. The second was a simple sequential file in which data were recovered by screening the file (in its entirety or partially) against a limited set of prescribed single dimensional criteria. The former had the advantage of almost unlimited flexibility at the cost of relatively high program administrative overhead. The latter had the advantage of simplicity and low overhead at the cost of longer search times and the possibility of its failing to satisfy some unforeseen sorting requirement.

Until such time as a sizeable quantity of test data are assembled, and one technique has clearly demonstrated its advantage over the other, both filing systems will be used.

3.3 STATISTICAL ANALYSES

Considerable effort was devoted to designing an experiment strategy to minimize the number of tests while maximizing the amount of pertinent information. The model of the manufacturing process incorporated 50 process steps and 27 chemical elements to be considered as possible contaminants at each process step. To evaluate only first-order effects, excluding all interactions, would require the solution of 1,350 simultaneous equations. To solve these equations deterministically, assuming no measurement errors and no factors overlooked, would require that a minimum of 1,350 wafers be processed. This was considered to be an unrealistic task to be accomplished in the time which was available. Alternatively, a stochastic approach was planned. Statistical tests of the data were planned to determine the relative significance of each variable. That is, a screening process was selected to determine which contaminants at which stations exhibited the largest effects on the dependent variable, yield. The results would show only main or first-order effects - only the sensitivity of yield to significant changes in the independent variables, contaminant levels. Initially, interactions between elements and second-order effects would not be analyzed. The screening would also serve to show the degree to which the product yield was dependent upon factors outside the experiment, that is, factors other than chemical contamination.

The screening process was designed to rank the independent variables in the order of most probable significance. This does not mean that any variable is to be excluded from the analysis, but simply that the probability of discovering highly significant variables early in the process will be enhanced. Initially, the ranking will be based upon the physical chemistry of the process. The most sensitive stations will be assumed to be those involving high processing temperatures since the adsorption rates of most elements are higher at elevated temperatures. On this basis it was assumed that the most critical process steps would be those involving and immediately preceding the formation of thermal oxide layers and P-N junctions. Process steps Nitride Etch P20 and Thermal Oxidation P25, for example, were ranked high on the priority list for early attention.

The system input is in the form of wafers which already have undergone a number of processing steps. From a statistical point of view, each wafer will have built-in variations as evidenced by such parameters as: resistivity of the substrate, thickness of epitaxial layer, resistivity, epitaxial run number, and orientation within the boule source. These variables are measured and recorded. The design of the experiment must account for these variations. This will be accomplished by block randomization and analysis of covariance.

As used in this context, block randomization is an experimental procedure that reduces experimental errors due to variability of the specimen. It will be accomplished by systematically mixing wafers with different initial properties to produce a homogeneous mix, rather than allowing a batch of wafers with relatively uniform but strongly biased initial properties to be processed. This mixing or randomization of batches of wafers will serve to reduce the experimental error due to specimen variability. Block randomization also will be used to control variability due to external factors such as personnel variability and processing variability, e.g., time, temperature, etc.

Analysis of covariance is an analytic procedure for controlling the effects of specimen variability by adjusting the observed response variables of the system for effects of the observed specimen variations. The procedure is a combination of analysis of variance and regression analysis.

In addition to specimen variability of the input, measurement of yield will be biased also by variability of processing characteristics. The electrical measurements, which will determine the final product acceptance, will be controlled carefully since variation in the measurements of these parameters could seriously affect yield figures and confound the response due to contaminant levels.

SECTION IV

PROGRAM SCHEDULE

4.1 PROGRAM STATUS

As of the end of February 1978, the project was approximately 10 weeks behind the schedule anticipated in the original planning and delineated in the project's PERT chart (refer to page 2-5/2-6 in the First Quarterly Report). That is to say, the project as of 28 February had achieved a majority of the planned objectives through 15 December 1977.

One cause for the delay was in training operators in the use of the spectrometer, which was originally thought to be the pacing item on the critical path. While the spectrometer was delivered on 16 December 1977, a month ahead of the schedule, the operators' training course scheduled by the manufacturer for 14-18 November for PRD and Microwave Associates personnel was postponed until 9-13 January, at which time Dr. George P. Allendorf of Microwave Associates was unable to attend.

It was expected that the time allocated for the course would be sufficient to train operators in the use of the instrument to a proficiency level where consistently accurate analysis could be performed. The course provided by the manufacturer was adequate for teaching the operator to turn on the spectrometer and operate it, but was inadequate in areas involving the preparation of standards, the generation of matrices (i.e., control computer operating programs), the analysis of organic materials, the aspiration of volatile liquids and making analyses at concentration levels approaching the resolution of the instrument.

Another cause of the delay was the excessive snowfall in the Northeast during January and February, which resulted in several days of plant closings at both Microwave Associates and PRD. These had a disruptive effect upon the project far beyond just the direct loss of man-hours. Microwave Associates was delayed in

finishing the construction of the laboratory area because of problems arising out of the need to coordinate such an activity with other moves within the plant, all of which were delayed by the weather. Because of the small staffs involved in the project, both at Microwave Associates and at PRD, any absences among the personnel had an extensive and profound effect upon progress of the work.

The inaccessibility of the software supplied with the spectrometer and the difficulty of coordinating modifications through the manufacturer to facilitate the automatic transmission of analytical data between the spectrometer in Burlington, Massachusetts, and the UNIVAC 1108 computer in Syosset, New York, indirectly delayed the project. While the lack of an adequate data transmission system did not curtail the operation of the spectrometer, the implementation of an alternate means of data transmission did occupy much of the time of the project's key personnel and thus delayed the project work.

As of the end of February 1978, the following tasks were completed:

1. The spectrometer was installed, demonstrated and accepted.
2. The manufacturing facilities were designated and scheduled, with the exception that the laboratory in which the spectrometric analyses were to be made was not completed.
3. The expendable materials were on hand with the exception of a few organic standards.
4. The ancillary instrumentation was at hand with the exception of a spectrum shifter needed to enhance the resolution of the spectrometer.
5. The experiments were designed.
6. The data communication link was installed but exhibited some malfunctioning.
7. The data management system was designed and programmed but not debugged.

8. The data reduction plan was developed but not programmed. (It was decided to make maximum use of existing statistical software program packages provided by UNIVAC and by the Biomedical Department of the University of California and programmed to run on the UNIVAC 1108.)

9. The analytical model was designed but not programmed.

10. An adequate staff of trained personnel was available at Microwave Associates to conduct the chemical analyses.

Before the "Analysis of Baseline" could be initiated, the following remained to be accomplished:

1. The preparation of a set of chemical solutions to be used as calibration standards.

2. Completion of the set of spectrometer control "matrices."

3. Techniques developed for the handling and analysis of organic chemicals.

4. Techniques developed for aspirating highly volatile liquids.

5. Techniques developed for sampling and analyzing gases, particularly where high flow rates were involved as in the gaseous reactors.

Before any automatic data processing could be initiated the following remained to be accomplished:

1. Preparation of computer programs for checking transmission errors in transmitted data in the absence of parity bits.

2. Preparation of computer programs for identifying, extracting and filing pertinent data.

3. Preparation of job control language programs for inputting statistical data into available statistical program packages.

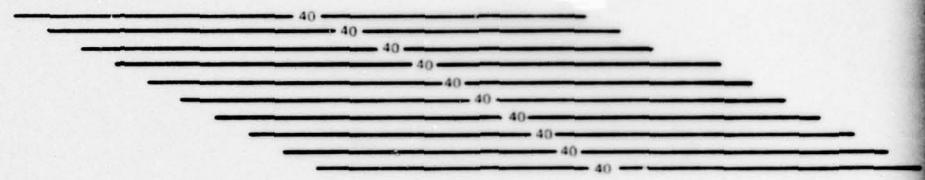
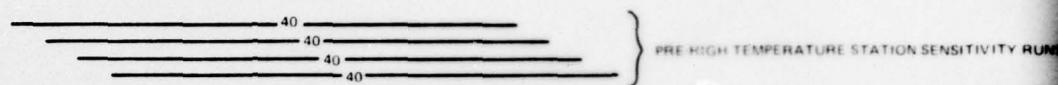
The program delays accrued through February 1978 were significant enough to warrant a major revision of the PERT plan.

In view of the delays encountered through the end of the second quarter, it was planned to develop and submit for approval a new PERT chart which would reorient the project's activities while holding to the project's major objectives and the submittal data for the final report. This would be accomplished by reducing the time allotted to Production Process Monitoring from nominally 15 weeks to 6 weeks and deferring the Development of System Specification so that it would be delivered after the project's final report.

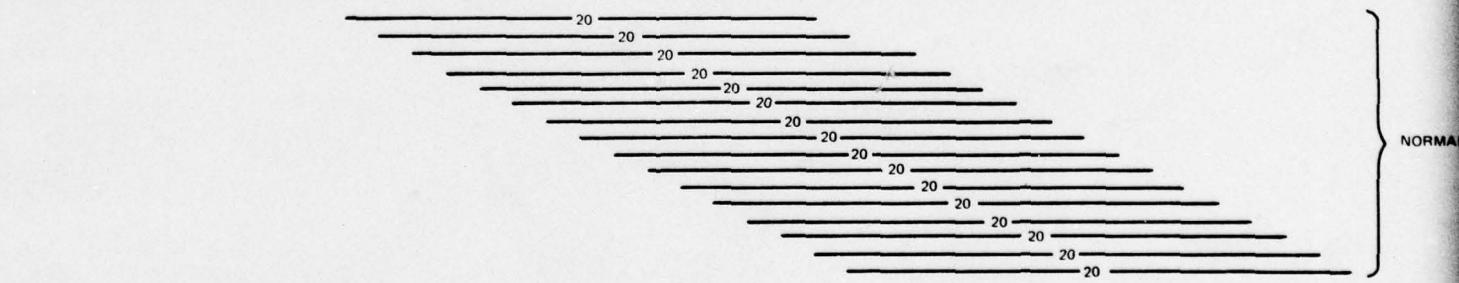
Until such time as a significant ensemble of analytical test data is assembled, the pacing item will be the manufacturing and testing of the PIN diodes. Figure 4-1, Wafer Processing Schedule, is a plan for acquiring those data. The plan calls for six series of wafers to be run. The first series of wafers, the Unperturbed Runs, will consist of not less than 20 wafers. It will be divided into 10 batches of two wafers each. A new batch will be introduced into the manufacturing process each day for 10 work days. These wafers will be processed as in a normal manufacturing operation except that more highly skilled technicians may be used to help resolve procedural problems which may arise from the imposition of the new and more exacting testing routines. Because only standard processing materials will be used in their manufacture and no reagent will be purposely contaminated or doped, the group will experience only incidental contamination.

The second series of runs, the Pre-High Temperature Station Sensitivity Runs, is designed to explore the effects of contamination in those operations which immediately precede operations performed at elevated temperatures. The plan is to start with a relatively large batch of wafers (say 40). The large batch will be processed as a unit in a normal manner up to the step under investigation. At that point the large batch will be divided into smaller batches, e.g., 20 sub-batches of two wafers each. Each sub-batch will be exposed to a different level of contamination during the processing operation. Upon completion of the operation the sub-batches will be reassembled into a single large batch and proceed through the remaining steps of the manufacturing process. The stratagem will permit one to correlate

APRIL														MAY																												
10	11	12	13	14	17	18	19	20	21	24	25	26	27	28	1	2	3	4	5	8	9	10	11	12	15	16	17	18	19	22	23	24	25	26	29	30	31	1	2	5	6	7



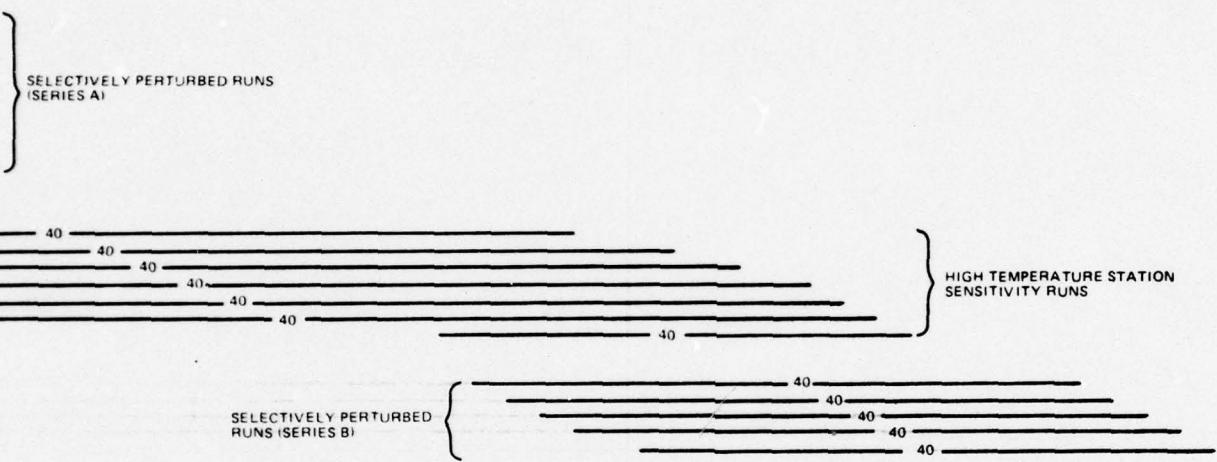
AUGUST														SEPTEMBER																									
10	11	12	13	14	15	16	17	18	19	21	22	23	24	25	28	29	30	31	1	2	3	4	5	6	7	8	11	12	13	14	15	18	19	20	21	22	25	26	27



NON-WORKING DAYS

JUNE																			JULY											
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31

SENSITIVITY RUNS



OCTOBER																			NOVEMBER																		
25	26	27	28	29	30	31	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31

NORMAL PRODUCTION RUNS

APPROXIMATE NUMBER OF WAFERS TO BE PROCESSED ~ 1380

Figure 4-1. Wafer Processing Schedule

2

4-5/4-6

directly the changes in yield to specific groups of contaminating elements at a specific process step or position. Refer to flow diagram in Appendix A. The second series will consist of four runs and will address Rinse P04, Rinse P11, Photoresist Stripping P19 and Rinse P24. It is planned to investigate the following nine groups of elements:

(1)	(2)	(3)
Lithium (Li)	Copper (Cu)	Magnesium (Mg)
Sodium (Na)	Iron (Fe)	Cadmium (Cd)
Potassium (K)	Gold (Au)	Calcium (Ca)
(4)	(5)	(6)
Silver (Ag)	Boron (B)	Phosphorus (P)
Zinc (Zn)	Aluminum (Al)	Arsenic (As)
Mercury (Hg)	Gallium (Ga)	Antimony (Sb)
(7)	(8)	(9)
Germanium (Ge)	Chromium (Cr)	Nickel (Ni)
Lead (Pb)	Molybdenum (Mo)	Manganese (Mn)
Tin (Sn)	Cobalt (Co)	Palladium (Pd)

A tenth sub-batch will be used as a control and will receive only incidental exposures. Two levels of concentrations of each of the nine groups of elements will be used, e.g., 10 ppm and 100 ppm.

The fourth series, the High Temperature Station Sensitivity Runs, will closely parallel those of the second series, the Pre-High Temperature Station Sensitivity Runs. They will address the high temperature operations directly. The series will include operating positions: Boron Deposit P05, Boron Diffusion P06, Boron Redistribution P07, Deposit Silicon Nitride P12, Etch Nitride (Plasma) P20 and Thermal Oxidation P25. Also included in this series, although run at room temperatures, is the final Clean P50.

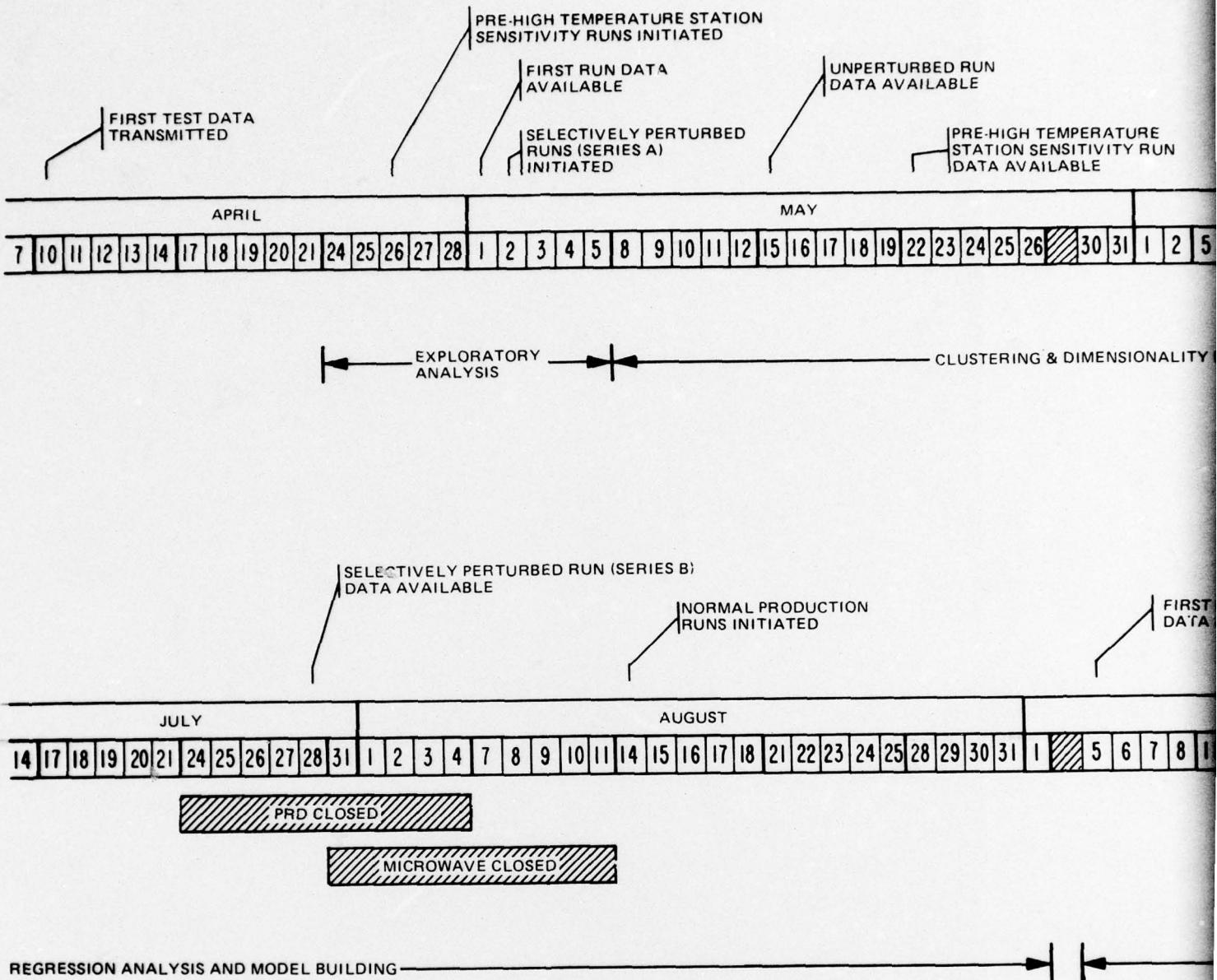
The fourth series presents some as yet unsolved implementation problems. Techniques for sampling and quantitatively measuring the contamination levels in high flux gases remain to be developed as do techniques for uniformly introducing controlled levels of contamination and subsequently purging the reactors.

The third and fifth series, the Selectively Perturbed Runs (Series A and B), are designed to address specific process steps which the statistical analyses will identify as critical to the building of the mathematical model.

The sixth and final series, the Normal Production Runs, like those of the first series will involve only incidental contamination. They will differ from the first series only in that they may use normal manufacturing personnel and procedures. The series will provide those statistics against which the mathematical model will be adjusted and verified.

It is planned to initiate the gathering of analytical data on or about 10 April 1978, at which time the first two-wafer batch of the Unperturbed Runs will be processed.

Consistent with the schedule for gathering the statistical data, the schedule for reducing the data and building the analytical model is presented as Figure 4-2, Data Reduction and Model Building Schedule. The reduction of the data and fitting of a model to the data must necessarily be a reiterative process of estimating and evaluating the factors which affect the yield. The steps of the process are outlined in Figure 4-3, Data Processing Flow Diagram.



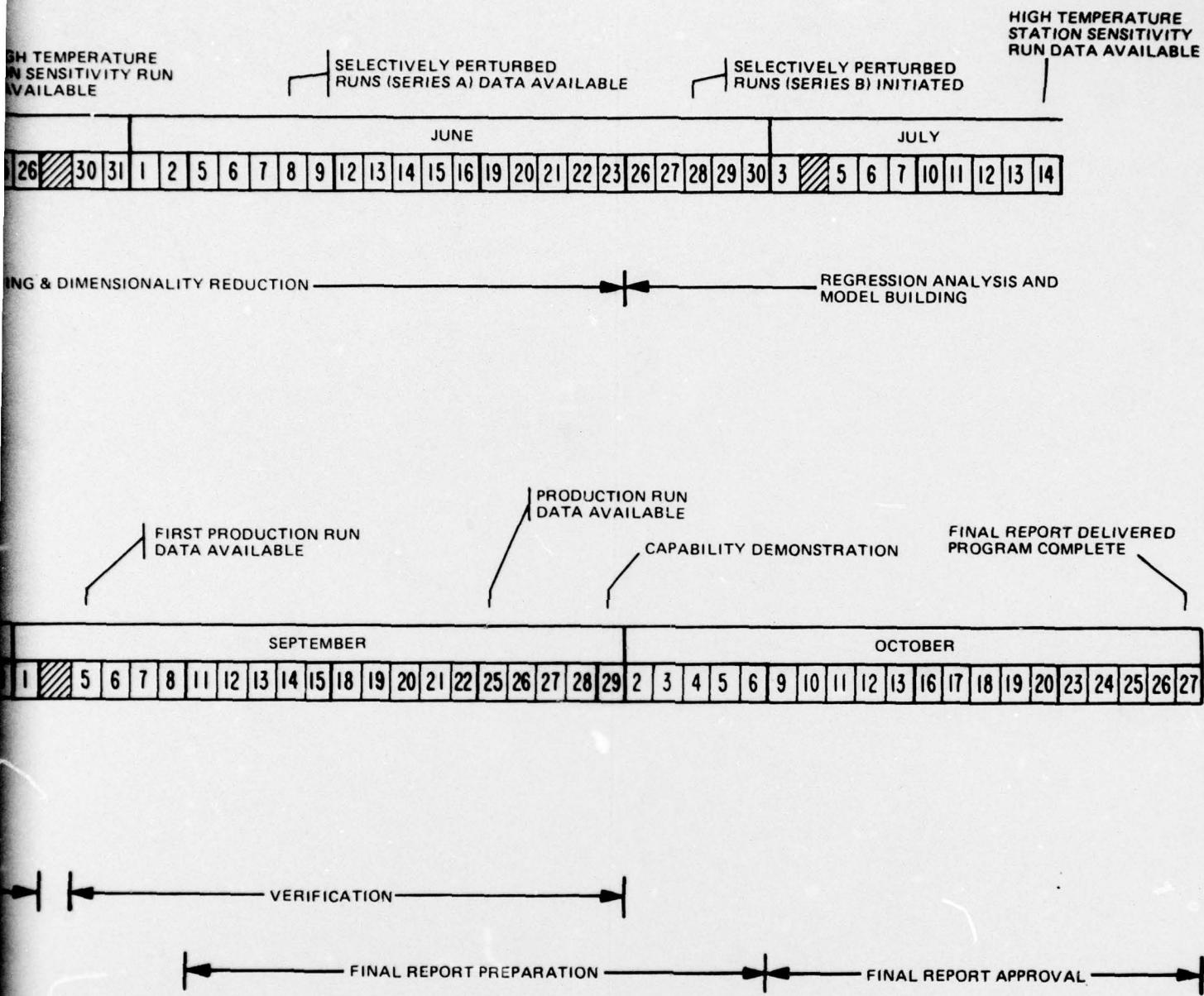


Figure 4-2. Data Reduction and Model Building Schedule

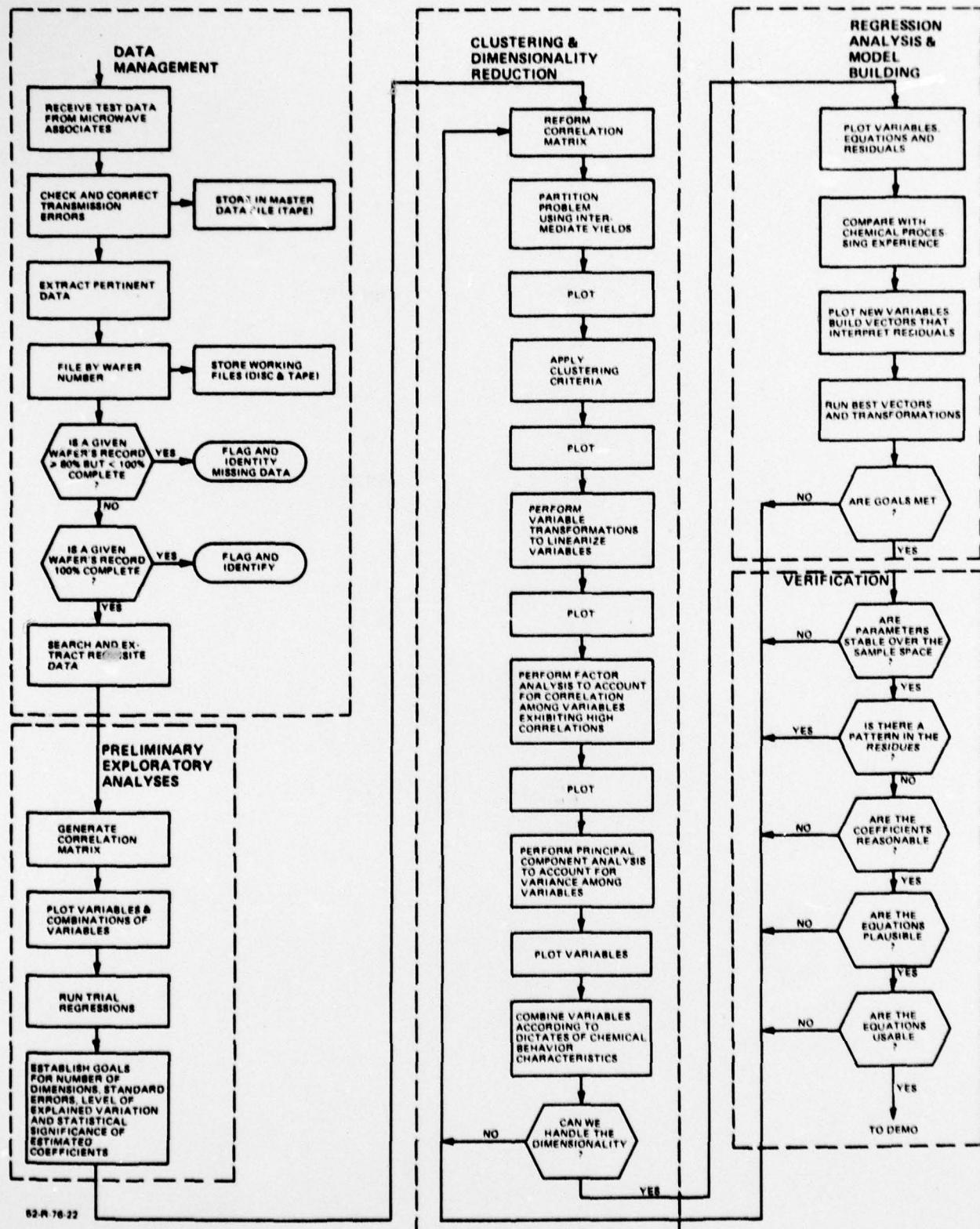


Figure 4-3. Data Processing Flow Diagram

SECTION V

FUTURE PROGRAM ACTIVITIES

5.1 PROBLEMS TO BE ADDRESSED IN THE THIRD QUARTER

A major problem which will be addressed early in the third quarter involves the analysis of organic materials, particularly those having high vapor pressures such as acetone. The molecular carbon species and complex ions present in the plasma of the spectrometer during the analysis of organic materials give rise to relatively high and variable background illumination. This, in turn, adversely affects the limits of detectability. The high vapor pressure, which most of the organic solvents of interest exhibit, create problems with the control of the aspiration rate of the sample into the plasma torch of the spectrometer.

To ameliorate the first of these problems, a dynamic spectrum shifter (Jarrell-Ash Model No. 90-555) will be procured and installed in the spectrometer. The device will allow an intensity measurement to be made at the peak of each spectral line, and then, by shifting the spectral blaze slightly, permit a measurement of the background intensity immediately adjacent to each line. The computer within the spectrometer will then compensate each intensity measurement for the background level at each spectral line.

To solve the second problem, a positive displacement pump will be added to the sample injection system of the spectrometer. This will be used to inject the sample into the nebulizer under positive pressure.

A third problem to be addressed during the early weeks of the third quarter will be to resolve procedural incompatibilities which remain in the interface between the spectrometer's computer, the cassette recorder, the Decwriter and the data line to the UNIVAC 1108 computer. These problems, while they are minor and presently do not impede the work of the project, are a source of annoyance and if unresolved will become significant when the volume of data to be transmitted increases.

and reaches its peak during the third quarter. Fortunately, all of these incompatibilities appear to be amenable to changes in software and operating procedures.

5.2 PROGRAM FOR THE THIRD QUARTER

The month of March 1978 will be devoted primarily to resolving the problems cited above and to establishing the accuracy of the spectral analysis. In the data reduction area, the time will be devoted toward readying the data management system and toward completing the search for effective statistical procedures which can be implemented on the UNIVAC 1108 computer.

The major thrust of the program during April and May will be directed toward the amassing of a statistical data base which will permit the correlation of measured electrical performance with analytical levels of trace-element contamination in the process reagents. During April and May, approximately 40 percent of the test data will be gathered. Some 820 wafers will be introduced into the manufacturing process of which approximately 380 will be completely processed. The wafers will be processed according to the schedule depicted in Figure 4-1, Wafer Processing Schedule.

The last week of April and the first week of May will be devoted to preliminary exploratory analyses of the test data as it is received from the processing of the wafers into PIN diodes. These steps are outlined in Figure 4-3, Data Processing Flow Diagram.

The remainder of May will be devoted to clustering and dimensionality reduction.

SECTION VI
PUBLICATIONS AND REPORTS

(There were no publications, conferences or talks made during the period covered by this report on or associated with the work performed under Contract No. DAAB07-77-C-0561.)

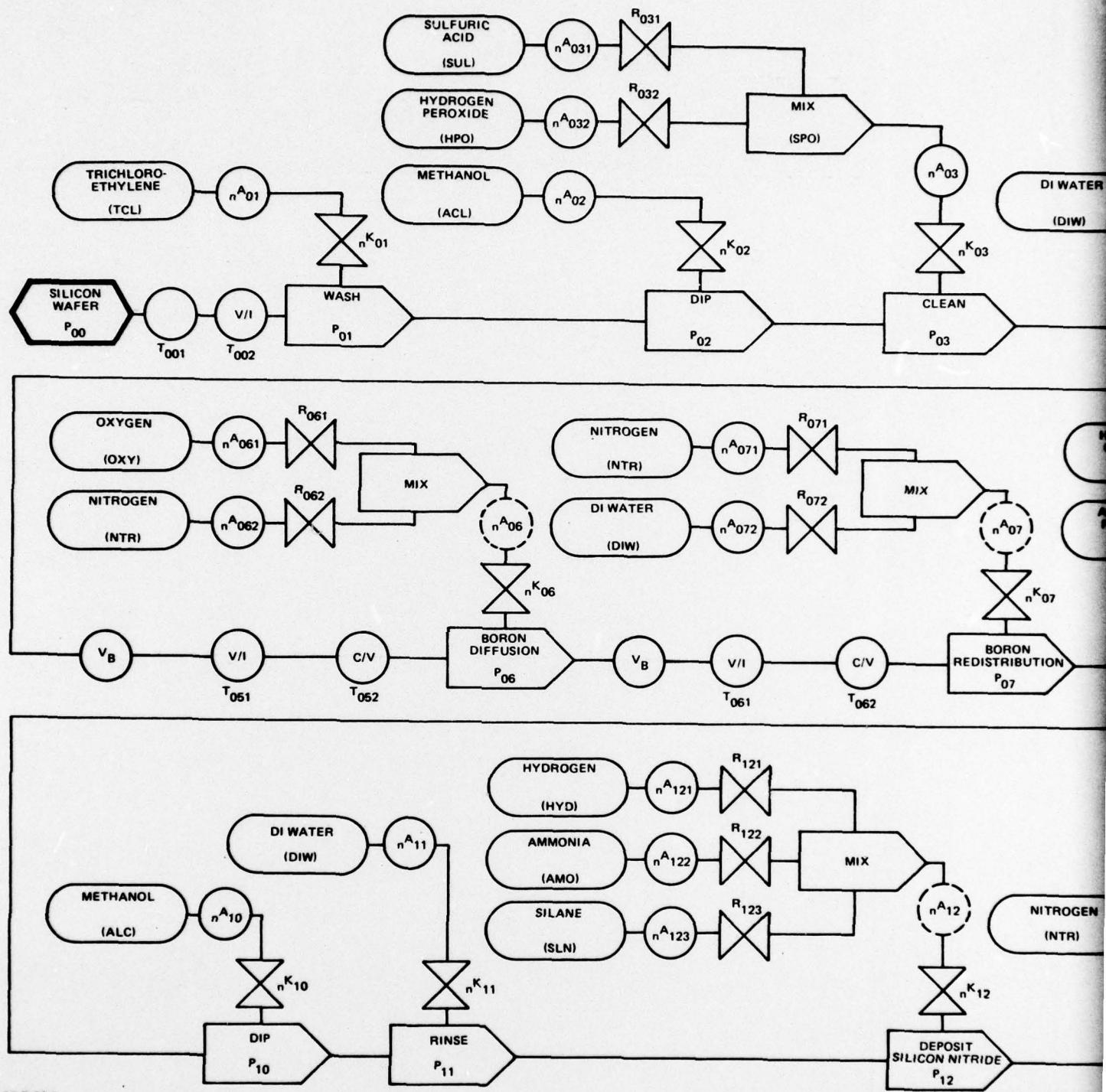
SECTION VII
PERSONNEL IDENTIFICATION

7.1 PERSONNEL ASSIGNMENTS

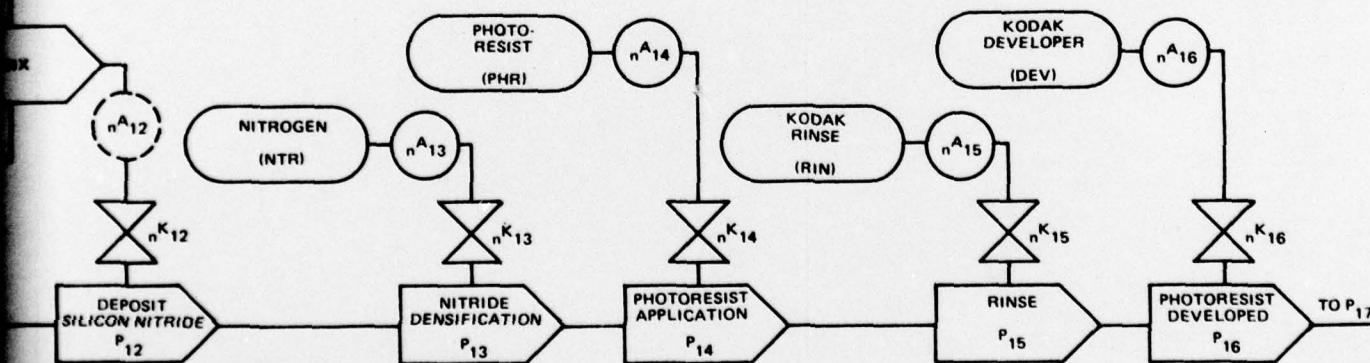
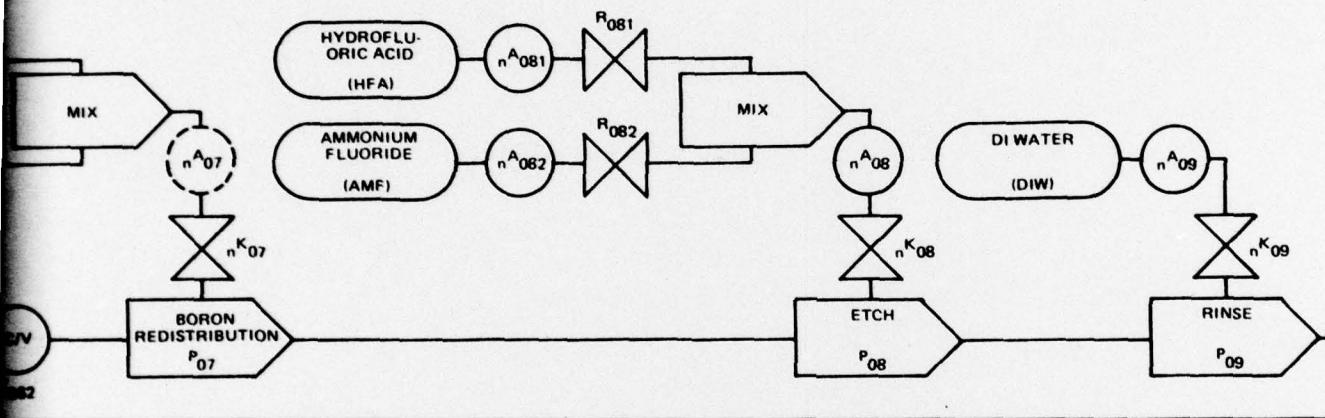
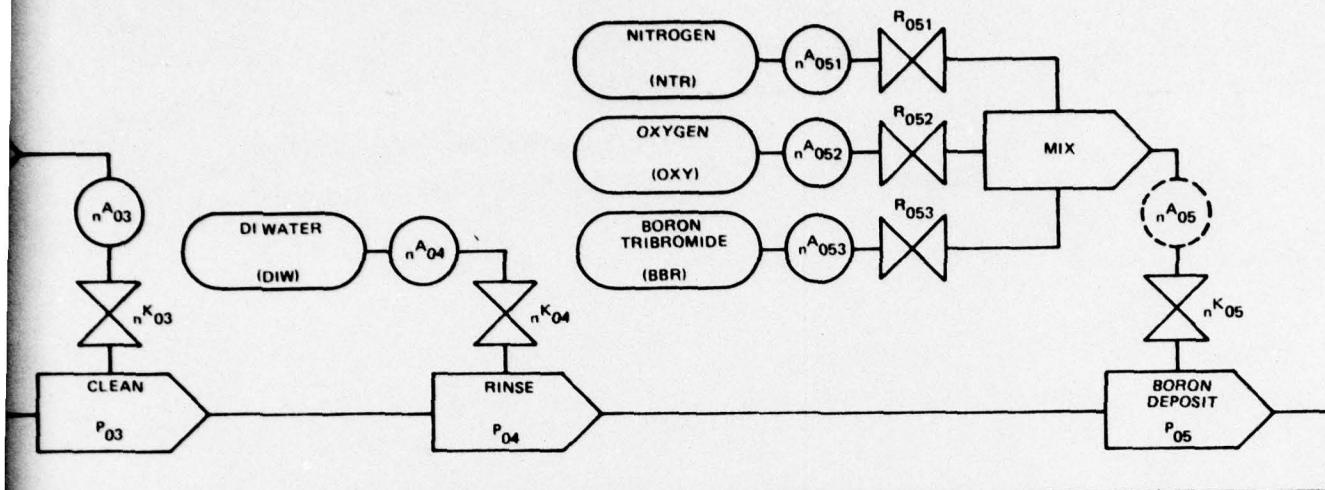
Persons working on the program and the hours worked through the report period were as follows:

<u>NAME</u>	<u>AFFILIATION</u>	<u>HOURS</u> <u>1ST QTR</u>	<u>HOURS</u> <u>2ND QTR</u>	<u>TOTAL</u> <u>HOURS</u>
Roy W. Spacie	PRD Electronics	408	560	968
Dr. George Allendorf	Microwave Associates	164	436	600
Albion Weeks	Microwave Associates	120	508	628
Dr. Demir S. Zoroglu	Microwave Associates		112	112
Peter Barnett	PRD Electronics		80	80
H. R. Bedrosian	Microwave Associates		30	30
Dr. David Levine	PRD Electronics		15	15

APPENDIX A
PIN DIODE MANUFACTURING PROCESS

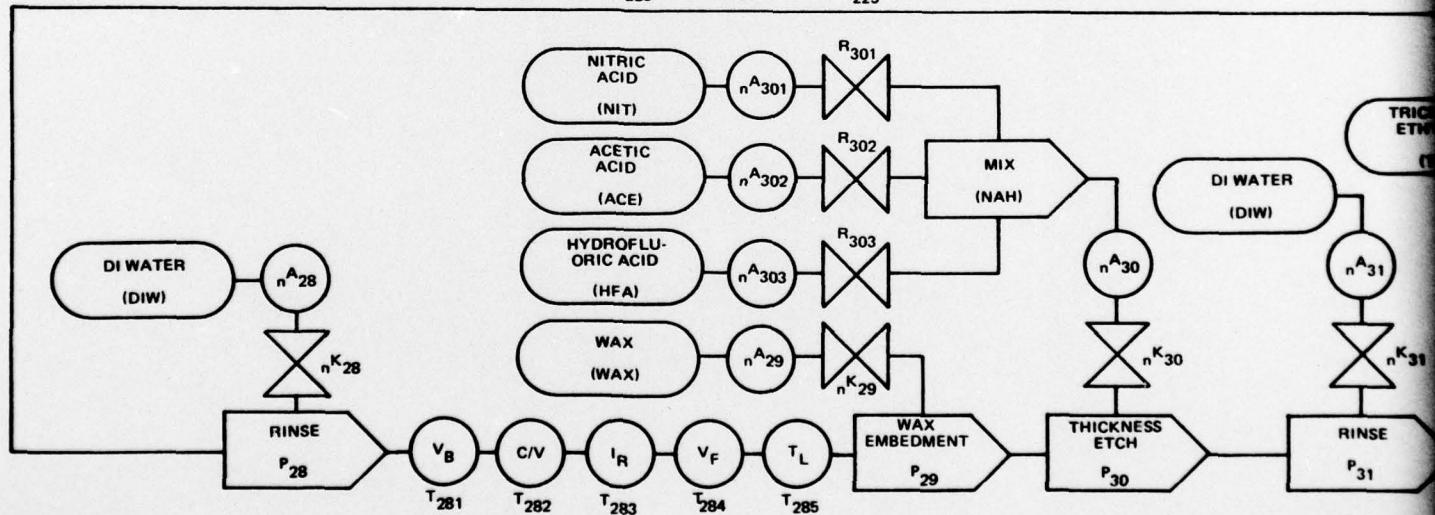
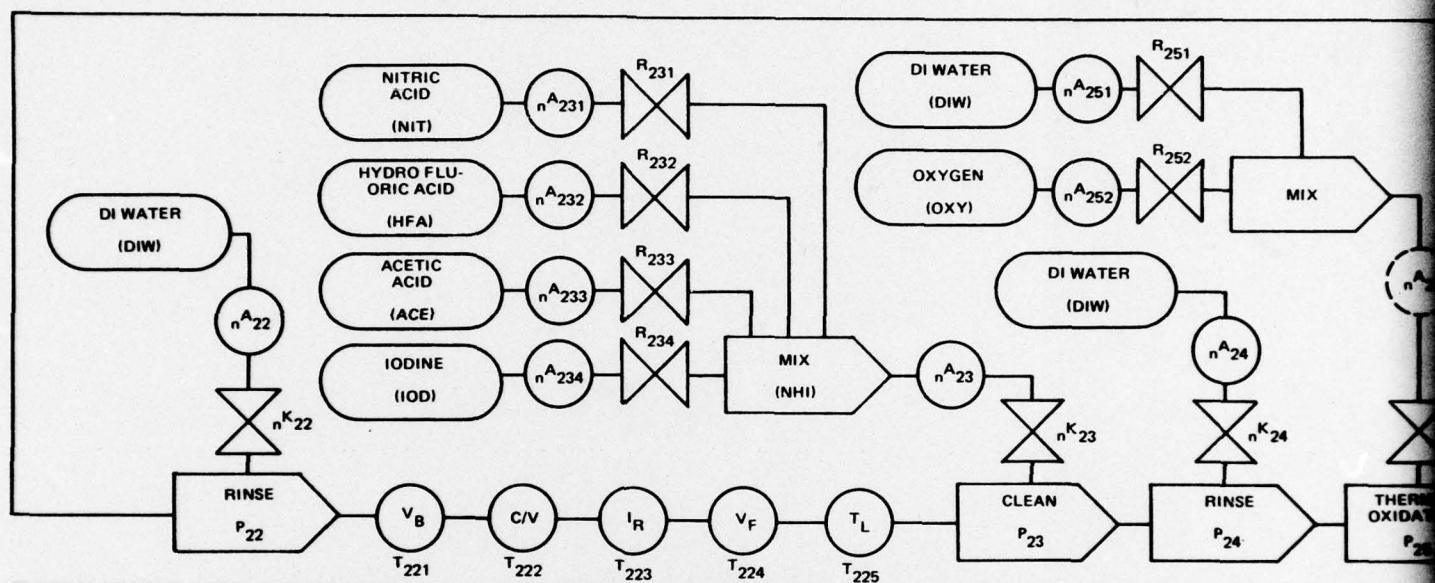
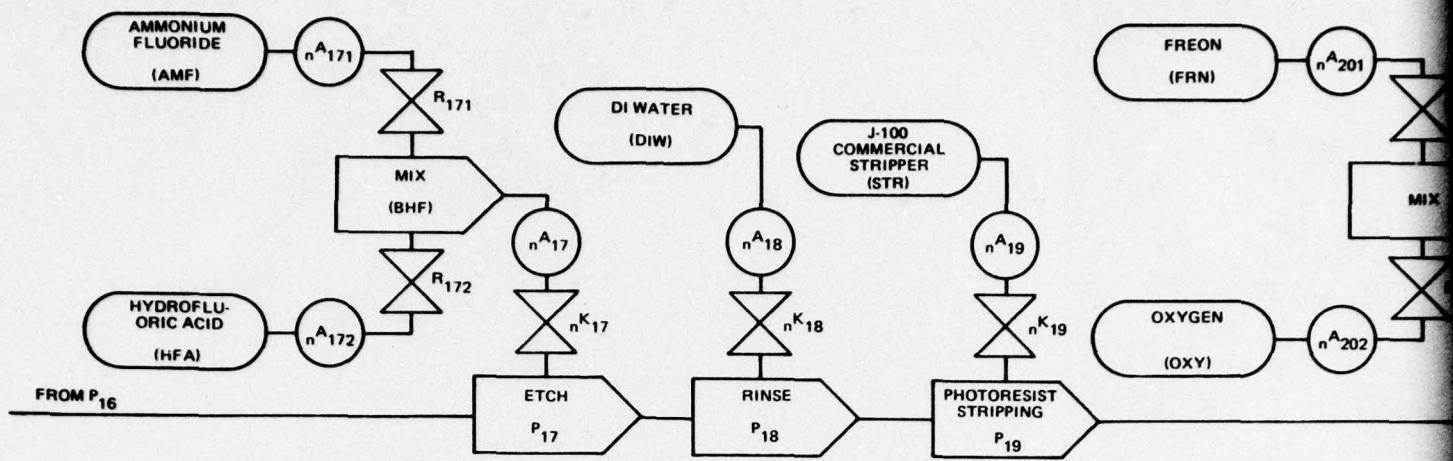


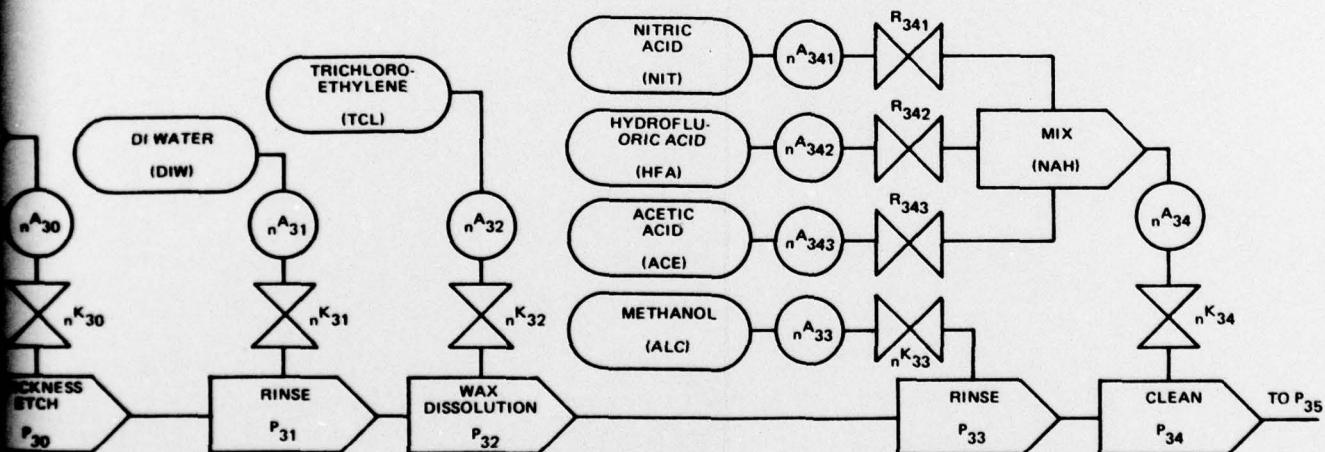
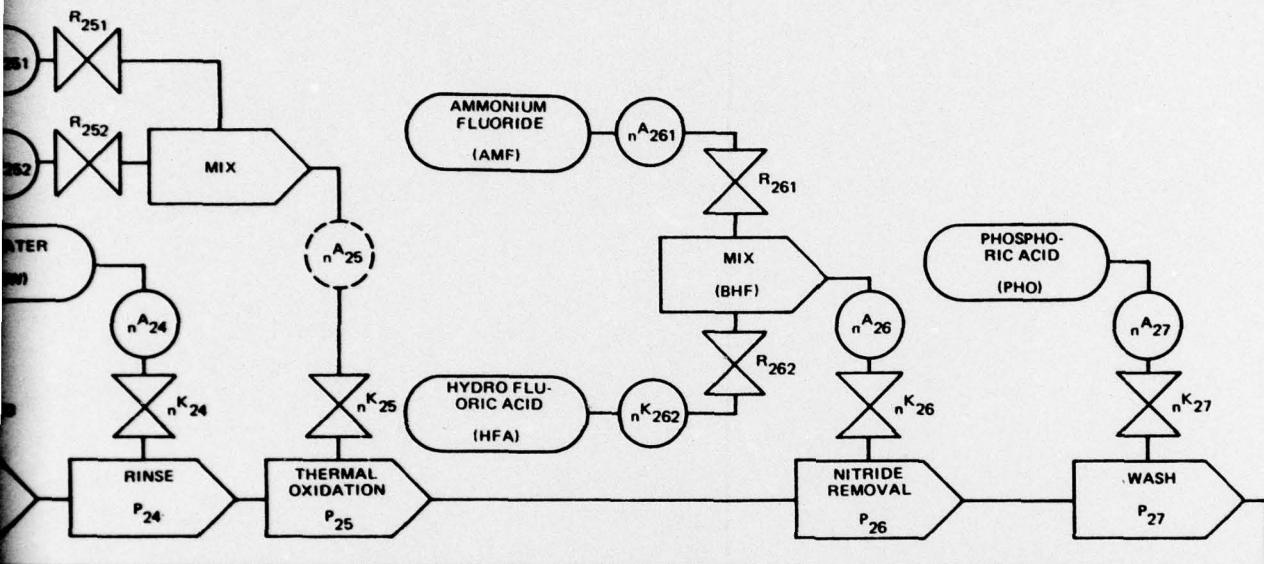
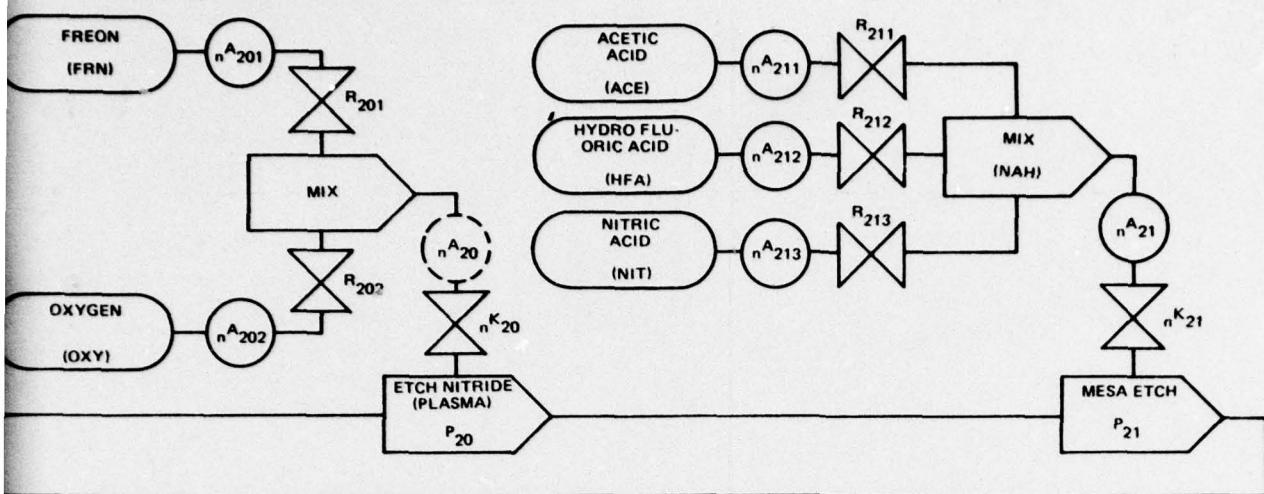
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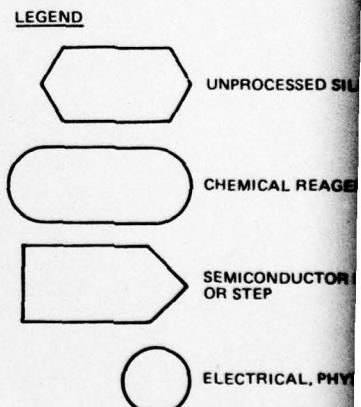
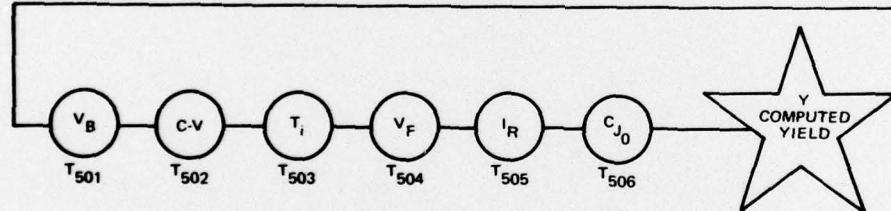
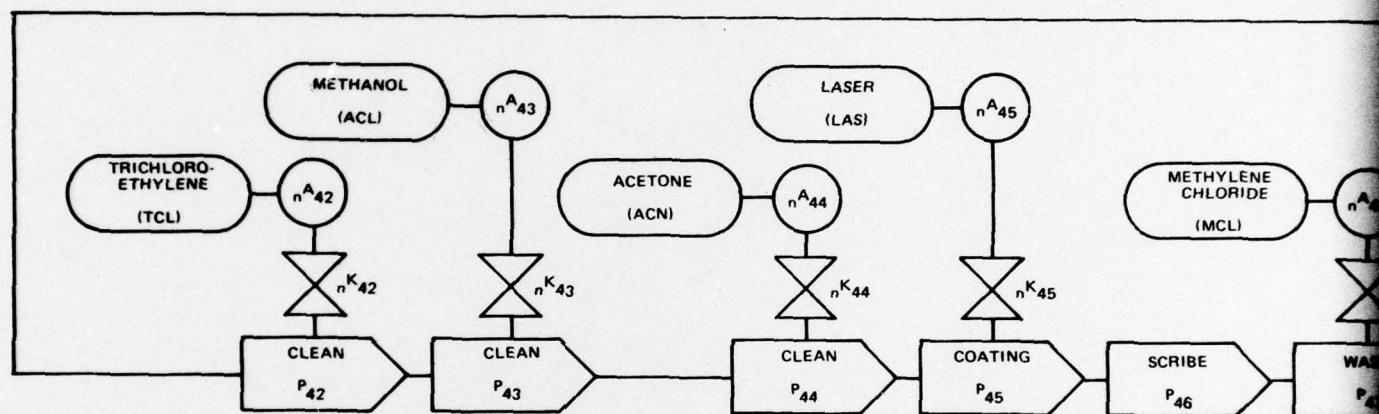
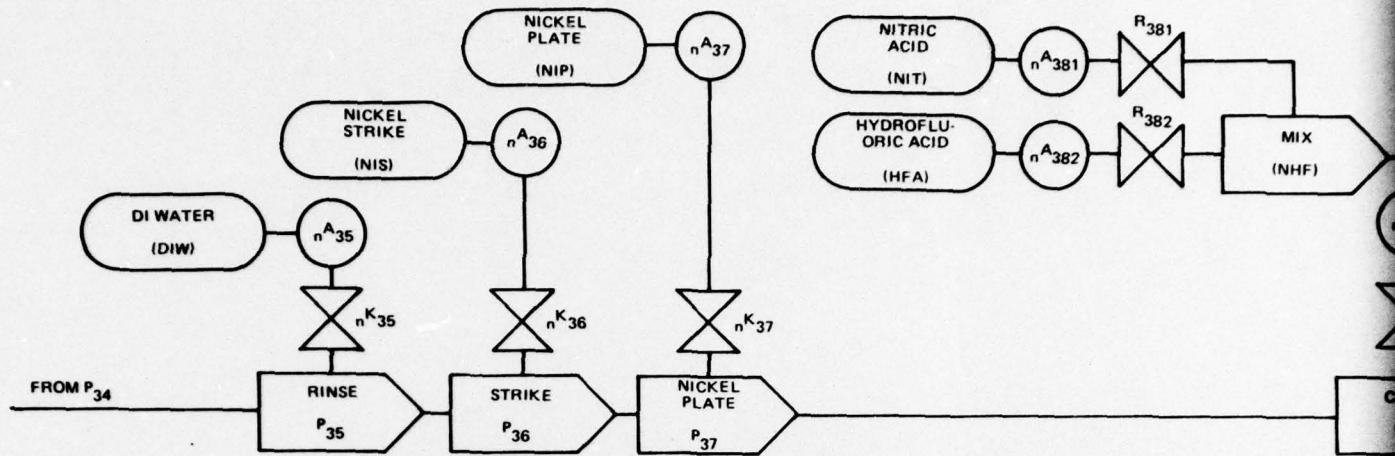
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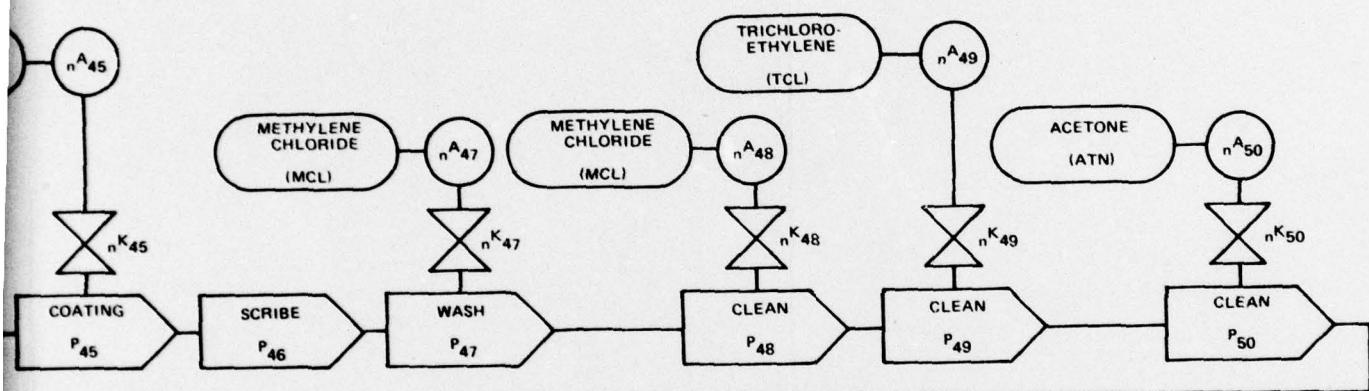
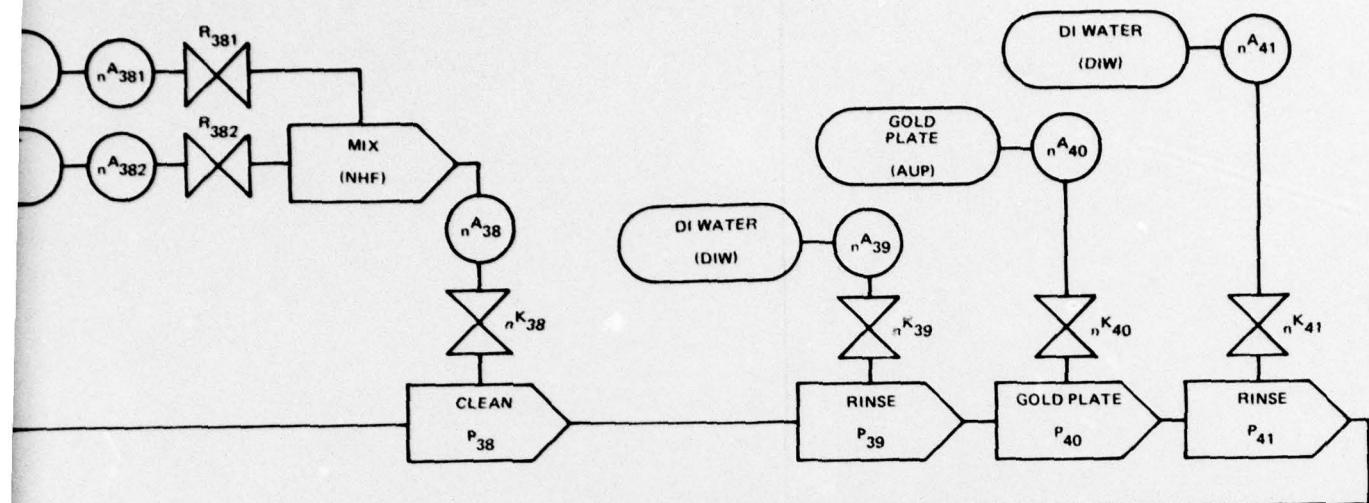
PIN Diode Manufacturing Process
(Sheet 1 of 3)



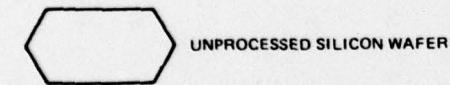


PIN Diode Manufacturing Process
(Sheet 2 of 3)

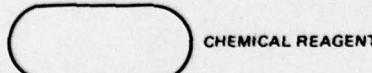




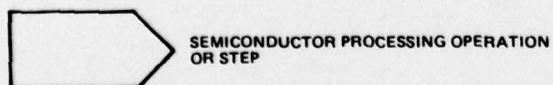
LEGEND



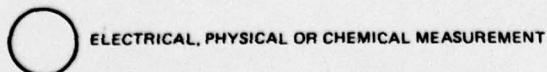
UNPROCESSED SILICON WAFER



CHEMICAL REAGENT



SEMICONDUCTOR PROCESSING OPERATION
OR STEP



ELECTRICAL, PHYSICAL OR CHEMICAL MEASUREMENT



COMPUTED OR DERIVED INDIRECT MEASUREMENT



TRANSFER RATIO OR COUPLING COEFFICIENT

P_{XX} - PROCESS STEP IDENTIFICATION

T_{XX} - ELECTRICAL TEST IDENTIFICATION

A - MEASURED OR DERIVED CONTAMINANT
CONCENTRATION LEVEL

K - VALUE OF TRANSFER RATIO



PIN Diode Manufacturing Process
(Sheet 3 of 3)